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POLYHYDROSILANES I. SYNTHESIS

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ABSTRACT

Using the well known Wurtz coupling technique, polyhydrosilanes copolymers with diphenyl - and methyl(phenyl) - sequences, were synthesised. This work describes the possibility to maintain stable Si-H group and to obtain in good yields, soluble, high molecular, functional polysilanes. IR, ^{1}H-NMR, ^{13}C, UV spectral data, quantitative elemental Si and H (from Si-H) analyses and indirect molecular weight investigation sustain the molecular structure of the copolysilanes.

INTRODUCTION

Organosilane polymers are known as precursors for β-SiC fibers [1-3], as impregnating agents for strengthening ceramics [4] and as dopable semiconductors [2]. Their properties lead to applications as photoresists, photoconductors, nonlinear optical materials, etc. [5,6,7] especially as a result of the influences of different kind of substituents. Therefore, electron donating or withdrawing groups could affect the electronic properties, hydrophilic or lipophobic groups could influence solubilities and surface properties, mesogenic groups in the polysilanic chain enhance anisotropic properties, etc.

Unfortunately, only a small variety of substituents can survive the action of molten sodium during the Wurtz coupling reaction: alkyl, aryl, alkenyl, dialkyl ethers [8]. This is the reason why the presence of the reactive side Si-H bonds could be used to increase the variety of substituents on polysilanes. A preparative method for polysilanes with Si-H groups is based on the dehydrogenative coupling of primary silanes with organosubstituted derivatives of transition metals as catalysts [9]. Using Wurtz coupling for Si-H polysilanes preparation seems to be unacceptable because of the great reactivity of the Si-H groups towards alkaline media. This paper shows that the polysilanes with Si-H pendant groups could be synthesized even in the harsh conditions of the Wurtz reaction, with good yields.

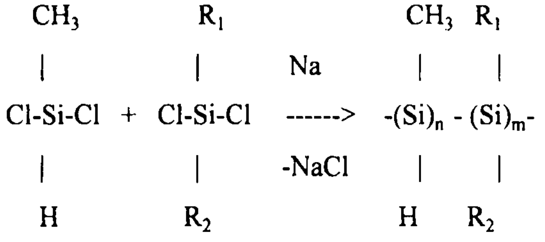
We describe the syntheses and characteristics of some copolymers containing diphenylsilylene and methyl(phenyl)silylene units together with methyl(H)Si-units.

EXPERIMENTAL

All the organodichlorosilanes were supplied by Merck. They were highly purified, by fractional distillation, prior to use.

Polyhydrosilane containing diphenylsilylene units (1).

To obtain the polyhydrosilane copolymer we used a conventional Wurtz coupling technique (Reaction scheme 1). A 500 mL, three-necked, round - bottomed flask was fitted with a reflux condenser, a pressure - equalizing addition funnel and a motor-driven stirrer. The sodium dispersion was made by mechanical high speed stirring of melted Na particles (10g, 0.4 mol) in dry toluene (120 mL) at gentle reflux for two hours, under dry N_2 athmosphere. A mixture of diphenyldichlorosilane (25.3 g, 0.1 mol) and methyl(H)dichlorosilane (11.5 g, 0.1 mol) in 30 mL dry toluene was added dropwise at a rate which maintained



$$\begin{array}{ccccc} CH_3 & & R_1 & & CH_3 \quad R_1 \\ | & & | & Na & | \qquad | \\ Cl\text{-}Si\text{-}Cl & + & Cl\text{-}Si\text{-}Cl & \text{------>} & \text{-}(Si)_n - (Si)_m\text{-} \\ | & & | & -NaCl & | \qquad | \\ H & & R_2 & & H \qquad R_2 \end{array}$$

$R_1 = CH_3$, C_6H_5 $n/m = r$

$R_2 = C_6H_5$

Reaction scheme 1.

vigorous refluxing. Care should be taken to exclude light from the reaction mixture, as the polymers are light sensitive and to maintain a dry, inert atmosphere. After the addition was complete, the mixture was refluxed for three hours then cooled over night and refluxed again for another two extra hours.Then the mixture was cooled to room temperature, quenched with a solution of 50 mL ethanol in 100 mL water and washed with 500 mL of distilled water. The organic layer and the solid insoluble polymer were separated using ultracentrifugation. Toluene was stripped of and the uncoloured oilish residue was dissolved in 50 mL of THF. From this solution, 10g of white solid polyhydrosilane were precipitated in 800 mL of methanol.

Synthesis of polyhydrosilane containing methyl(phenyl)silylene units (2) was made using the same technique and the same quantities (0.1 mol of methyl(phenyl)dichlorosilane and 0.1 mol of methyl(H)dichlorosilane, molar ratio 1:1). Finally 9 g of solid polyhydrosilane white product were obtained by precipitation from 1000 mL ethanol.

Fractionation of the copolymers was made by adding increments of isopropyl alcohol to the THF solutions of the polymers. IR spectra were registered with a Perkin - Elmer 457 spectrometer in the region of 3000 - 400 cm^{-1} on KBr pellets.

Proton and ^{13}C-NMR spectra were determined with an AC-80-Bruker spectrometer, on polymer solutions in carbontetrachloride (copolymer 1) and deuterochloroform (copolymer 2). The ratio Si-H to SiXY units in the polymer (r) was obtained by integration of the NMR signals for the different groups.

UV spectra were determined in chloroform with a Specord M-42 spectrofotometer. Inherent viscosities were measured in dry toluene at 25°C using a Cannon - Ubbelohde viscometer. Si and H (from Si-H groups) elemental analyses were performed according to standard procedures (decomposition of the polymer sample with strong acids for Si, and reaction with 0.5% KOH solution in ethanol for H).

RESULTS AND DISCUSSION

The polyhydrosilane copolymers were obtain by the cocondensation Wurtz reaction of $XYSiCl_2$ to $Me(H)SiCl_2$, molar ratio = 1:1, with sodium dispersion in toluene.The ratio of Me(H)Si to Ph_2Si units is, according to the spectral data , r = 1:1.Me(H)Si to MePhSi ratio is lower than the ratio of comonomers used in the synthesis (r = 0.8).

Yields, inherent viscosities, elemental Si and H (from Si-H) analyses, and ratios of Si-H to SiXY for the copolymers are shown in Table I. The yields of soluble copolymer, are similar with those for the coresponding homopolymers with the same XYSi groups.

To prevent any hyrolitic secondary reactions we worked under dry nitrogen atmosphere and used a large excess of sodium to destroy all the Si-Cl bonds in the mixture. The formation of a small quantity of insoluble material is probably a consequence of the high cristallinity of the products.

TABLE I

Yields, h_{inh} ,Si and H Elemental Analyses and Si-H to SiXY ratios of the Copolymers

Copolymer	Yield (wt %)		h_{inh} (dL/g)	Si (%)	H (%)	r (monomer ratio in the copolymer)
	insol	sol				
(1)	5.5	27.1	2.35	23.50	0.44	1.00
(2)	7.8	21.2	3.20	33.06	0.58	0.80

A very important observation is that the Si-H bonds were stable during the reaction. Even in the final phase when small amounts of alcohol - water mixture were added (to discharge any excess sodium and dissolve sodium chloride) no H_2 emission was observed. This seems to be a consequence of the reaction mechanism complexity which needs further clarifications.

Even though the backbone is comprised solely of sigma bonds, all of the polysilane derivatives absorb strongly in the UV spectral region. The literature [10,11] mentioned that polysilanes containing aromatic groups directly bonded to the backbone were significantly red shifted probably due to the conjugative interactions between phenyl substituents and the silicon chain and to the increased chain length of copolymers. In our case both polyhydrosilanes have phenyl groups in the backbone and high molecular weights and for these reasons λmax_{Si-Si} = 320 nm for copolymer (1) and λmax_{Si-Si} = 328 nm for copolymer (2).These results are consistent with data reported for several linear silane oligomers [14].

The infrared spectra and absorbtion assignments (Table II) are in agreement with the expected polymeric structures [12,13].The Si-H absorption maxima is present at 2100 cm^{-1}.

TABLE II

Infrared Absorptions

Absorption (cm^{-1})			
Copolymer	(1)	(2)	
	3060(w)	3000(w)	CH (phenyl)
	3050(w)	3070(m)	
		2980(m)	CH
		2860(w)	
	2100(m)	2105(m)	Si-H
	1450(m)	1455(m)	Si-Ph
	1250(w)	1250(m)	Si-CH$_3$
	1100(m)	1100(s)	Si-Ph
	870(m)	880(m)	Si-CH$_3$
	740(s)	750(s)	
	700(s)	705(s)	Si-C
	500(w)		Si-Si
	470(m)	460(m)	

The ^{1}H and ^{13}C NMR spectral data and assignements of the copolymers are listed in Table III. For this kind of copolymers the methyl proton resonances were exceptionally broad as a consequence of some overlapping peaks. This broadening of the proton signals increase with increasing molecular weight and phenyl content similar with other polysilane homopolymers [13, 15]. Aryl groups attached to silicon have the effect of shielding of nearby protons.

Indirect molecular weight estimations were made comparing inherent viscosity of poly(dimethyl-co-diphenyl)silane (η_{inh}= 5.35dL/g) with inherent viscosities of the synthesised polyhydrosilanes (Table I). Therefore it is

TABLE III

^{1}H and ^{13}C NMR Chemical Shifts

Copolymer	H (ppm)	C (ppm)	Assignement
(1)	0.28(m,vb)	-5.19(m,vb)	Si-CH_3
	5.28(b)		Si-H
	7.27(m,vb)	23.2(m,b),130.7(b) 135.9(b), 138.0(b)	Si-C_6H_5
(2)	0.50(m,vb)	-10.02(m,vb)	Si-CH_3
	3.55(b)		Si-H
	7.15(m,vb)	127.01(m,b),127.8(b) 135.5(b), 135.8(b)	Si(C_6H_5)

possible to estimate that both polyhydrosilanes had lower molecular weights than a classic term of the copolysilanes series.

All these copolymers are white powders with softening points between 70°-120°C (1) and 100°-150°C (2). TGA tests in nitrogen were made to obtain the onset temperature, the temperature at which further degradation ceases, and the wt% residue as follows: for copolymer(1), 300°C and 738°C and 36%; for copolymer(2), 310°C and 690°C and 50%. Both copolymers are soluble in THF, chloroform, toluene, benzene and can be casted into thin films very well.

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