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HYDROSILNAPHTHALENE-SILOXANE COPOLYMERS

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ABSTRACT

Silnaphthalene-siloxane copolymers with reactive Si-H pendant groups were synthesized through the cohydrolysis reaction of 1,4- bis(hydrochlorosilyi)naphthalene with dimethyl-,methyl-(phenyl)-, and diphenylchlorosilanes. Allproducts were characterized by IR,'H-NMR, Si and H elemental analysis,and molecular weights estimations.

INTRODUCTION

Polysilarylenesiloxanes are copolymers for specific applications resulting from their high thermal stability. Merker [1] was the first to synthesize segmented copolymers containing poly(tetramethyl-p-silphenylene) and polydimethylsiloxane using hydroxy-terminated monomers and oligomers. In the mid 70's, the synthesis and the characterization of some siloxane-silarylenesiloxane segmented copolymers was investigated in order to develop new polymeric materials for sealant and seal applications within wide temperature range, good chemical/fuel resistance, high temperature stability, low temperature flexibility, adhesion to metal substrates and processability [2]. Functional siloxane-silarylenesiloxane copolymers were synthesized for improving some of their physico-chemical properties. Thus, Pittman [3] studied poly(arylenesiloxanes) with ferrocene pendant groups and Nagase [4] obtained high molecular silarylene copolysiloxanes with pendant double bonds. The present work deals with the cohydrolysis reaction of bis(hydrochlorosilyl)naphthalene with chlorosilanes containing methyl- or/and phenyl substituents at silicon atoms in order to obtain silnaphthalene-siloxane copolymers with reactive pendant Si-H bonds.

EXPERIMENTAL SECTION

Spectra

^{1}H-NMR spectra were obtained on a JEOL 80 MHz spectrophotometer using CC1^4 as solvent and tetramethylsilane as internal standard. IR spectra were recorded on a Perkin-Elmer spectrophotometer in the 400-4000 cm-'^{1} region using KBr pellets.

Inherent viscosities (η) were determined at 25°C in toluene, using a Canon Ubbelohde viscometer.

Materials

Methyldichlorosilane (98.5% wt.), dimethyldichlorosilane (98.5% wt.), methyl(phenyl)dichlorosilane (99.2% wt.) and diphenyldichlorosilane (98.5% wt.) were supplied by Merck. Naphthalene (98.5% wt.) was obtained from Fluka. All chlorosilanes were freshly distilled before use.

Synthesis of 1,4-dilithium-1,4-dihydronaphthalene (DLDHN)

A 250 mL three-necked, flat bottomed reaction flask, was carefully dried, and then charged with a stirring bar, 10 g (0.07 mol) pure naphthalene, 50 mL diethyl ether previously dried over Na wire, 2 g (0.28 mol) lithium in small grains and sealed. The mixture was stirred at ambient temperature for 90 hours [5]. The dark red ethereal solution of 1,4-dilithium-1,4-dlihydronaphthalene was for immediate use.

Synthesis of 1,4-bis(methylhydrochlorosilyi) naphthalene oligomer (MHCSN)

An identical reaction flask equipped with a stirring bar, reflux condenser, argon inlet, and a dropping funnel was carefully dried and then charged with 0.20 mol methyldichlorosilane dissolved in 50 mL anhydrous diethyl ether. The DLDHN solution in diethyl ether was added dropwise with vigorous stirring avoiding overheating due to the reaction's exothermal effect. White solid LiCl slowly separated during the reaction. Stirring was continued for an additional hour.

Finally, the mixture was refluxed for another 60 min. in order to ensure the complettion of the reaction and then cooled to room temperature. The unreacted lithium grains and LiCl were filtered under positive argon pressure and the excess of methyldichlorosilane and the solvent were stripped off. An amount of 8 g dark yellow product was obtained. Yield: 35%.

Copolymers synthesis

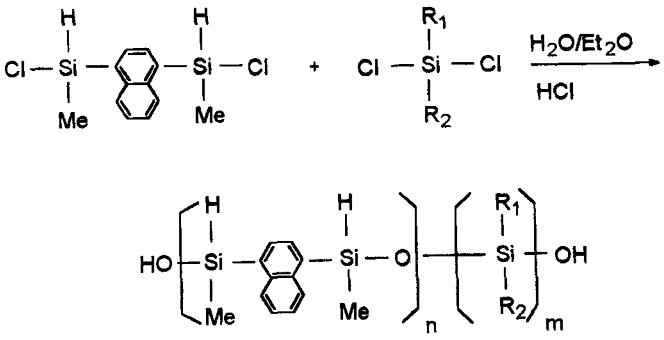
A 250 mL three-necked round-bottomed flask was fitted with a reflux condenser, a dropping funnel and a mechanical stirrer. A solution of 5 mL water in 100 mL diethyl ether was introduced into the reaction flask. A mixture of 0.024 mol MHCSN and 0.024 mol organodichlorosilane in 50 mL anhydrous diethyl ether was added dropwise, maintaining a temperature of 20°C (addition required 0.5 hours). The reaction was completed when no significant variations of the reaction mixture's viscosity were registered. The solution was then washed up to pH=6.5 and dned on Na_2SO_4. The solvent was then distilled and the remaining product was processed as follows:

- Reaction of MHCSN with dimethyidichlorosilane (DDS). An oilish-like product resulted which was stripped under 5 mm Hg pressure, in order to eliminate the low boiling fractions due to the secondary autocondensation reactions of DDS. Finally, 7 g of a light yellow liquid product were obtained. Yield 70%.
- Reaction of MHCSN with methylphenyldichlorosilane (MPhDS). Five grams of a dark yellow viscous product remained after volatile fractions' distillation, Yield 45.4%.
- Reaction of MHCSN with diphenyldichlorosilane (DPhDS). The greasy· residue was dissolved in 50 mL THF. Excess methanol (800 mL) was then added to the THF solution while stirring to precipitate the polymer. The precipitate was dned in vacuum (5 torr) at 110°C for 4 hours. Yield: 3.5 g; 2 7%.

RESULTS AND DISCUSSION

Hydrosilylnaphthalene-siloxane copolymers were obtained through the cohydrolysis reaction of 1,4-bis(methylhydrochlorosilyl)naphthalene oligomers with dimethyl-, methylphenyl-, and diphenyldichlorosilanes (Reaction Scheme 1). This procedure leads to random copolymers.

1,4-(methylhydrochlorosilyl)naphthalene synthesis was presented as a coupling reaction of 1,4-dilithium-dihydronaphthalene with $Me(H)SiCl_2$ (Reaction Scheme 2) avoiding H_2O contamination.



Copolymer:

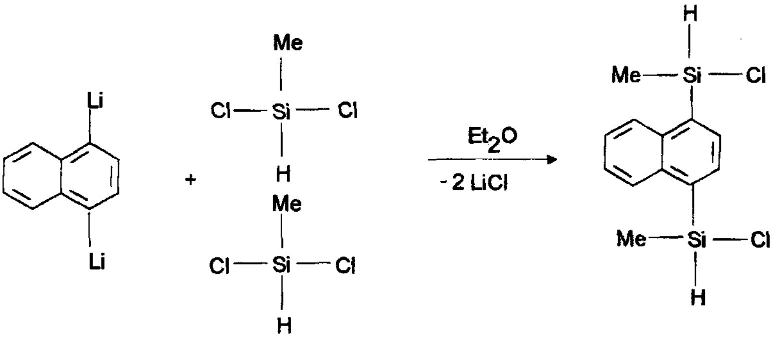
(1) $R_1 = CH_3$, $R_2 = CH_3$

(2) $R_1 = CH_3$, $R_2 = C_6H_5$

(3) $R_1 = C_6H_5$, $R_2 = C_6H_5$

n / m = r

Reaction scheme 1



Reaction scheme 2

MHCSN physico-chemical properties:

B.p. = 210 - 211.5°C (1 mm Hg); $n^{20} = 1.5661$; $d^{20} = 1.0576$ g/cm^3

MHCSN elemental analysis (calc./found)

Si (% wt.) 19.5 / 19.00; H (% wt.) = 0.69 / 0.80 (from Si-H)

Cl (% wt.) 24.73 / 25.33

Table 1

Yields, Inherent Viscosities and Compositions of the Copolymers

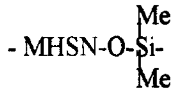
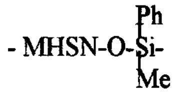
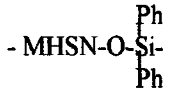
No.	Unit	Yield (wt.%)	η (dL/g)	r
1.	 $-\mathrm{MHSN{-}O{-}}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-$	70.0	0.20	0.25
2.	 $-\mathrm{MHSN{-}O{-}}\overset{\mathrm{Ph}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-$	45.4	0.41	0.47
3.	 $-\mathrm{MHSN{-}O{-}}\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{Si}}}-$	27.0	0.72	0.43

Table 2

Infrared Absorptions of Copolymers

Absorption (cm^{-1})			Assignement
(1)	(2)	(3)	[6]
3500	3490	3490	OH
3085-3050	3090-3050	3090-3050	CH (aromatic)
2960-2940	2958-2930	2958-2930	CH
2150	2150	2150	Si-H
1600	1610	1610	aromatic ring
1480	1500	1500	aromatic ring
1420	1430	1430	Si-Ph
1260	1255	1260	Si-CH_3
1050-1100	1050-1100	1050-1100	Si-O
850-900	860-900	860-900	$(Si)_2$Naphthyl
750	760	750	Si-CH_3
520	510	510	Si-O

Molecular weight was obtained by cryoscopic measurements in benzene: 287.00 calcd./ 288.52.

Yields, inherent viscosities, and ratios of comonomers (r) for the synthesized copolymers are listed in Table 1. The evaluation of these data suggests that in the case of MHCSN-DDS the reaction proceeds mostly as an autocondensation, the growing chain reacting preferentially with the dimethylstlyl units at first, and then with the hydrosilylnaphthyl units.

As for the other products, the reactivities of the active sites in the reaction mixture were balanced and the content of the backbone in methylhydrosllylnaphthyl units become significant.

Table 3
^{1}H-NMR Chemical Shifts (ppm)

Copolymer Assignement [6]	(1)	(2)	(3)
$-CH_3$ Si-Me	0.15 (s)	0.38 (s)	-
$-CH_3$ Si(H)-Me	0.21 (s)	0.20 (s)	0.20 (s)
-H Si-H	4.75 (s)	4.78 (s)	4.75 (s)
-H Si-OH	5.55 (s)	5.62 (s)	5.62 (s)
$-C_6H_5$ Si-Ph	-	7.27 (m)	7.25 (m)
$-C_{10}H_8$ $Si-C_{10}H_8-Si$	7.83; 7.75; 7.52 (m)	7.85; 7.75; 7.52 (m)	7.82; 7.71; 7.50 (m)

Table 4
Si and H (from Si-H bonds) Elemental Analysis

Compound	Calcd. / found (wt.%)	
	Si	H (Si-H)
(1)	34.83/34.11	0.23/0.18
(2)	23.09/22.81	0.44/0.52
(3)	19.23/19.03	0.39/0.28

Characteristic IR absorption bands are displayed in Table 2.

The Si-H absorption band is present very clearly at 2150 cm-^{1} in all products. The Si-O-Si bond absorbance exhibits the same intensity in all copolymers sustaining the presumed reaction scheme.

Infrared spectra and absorption assignments are in agreement with the expected polymeric structures. The content of hydrosilylnaphthalene units in copolymers was determined from integration of the peak area in the ^{1}H-NMR spectra (Table 3) and by elemental H (from Si-H groups) and Si analysis (Table 4).

A peak at aproximately 4.75 ppm in ^{1}H-NMR spectrum was assigned in all linear copolymers to the proton from SiH group.

The peak areas of phenyl and naphthyl protons were collected from the regions of 7.25 to 7.27 and 7.50 to 7.85 ppm respectively.

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