

AD-A085 202

UNION CARBIDE CORP TARRYTOWN N Y  
ORGANOSILANE POLYMERS. III. BLOCK COPOLYMERS. (U)  
APR 80 J P WESSON; T C WILLIAMS

F/6 11/9

N00014-75-C-1024

UNCLASSIFIED

TR-79-1

ML

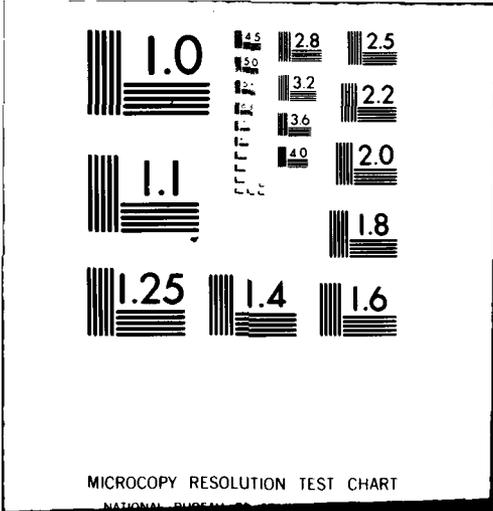
101

55

■



END  
DATE  
FILMED  
7-80  
DTIC





Office of Naval Research

Contract N-00014-75-C-1024  
Technical Report 79-1

Organosilane Polymers, III: Block Copolymers

by

J.P. Wesson and T.C. Williams

Union Carbide Corporation  
Tarrytown, New York 10591

SEARCHED  
SERIALIZED  
INDEXED  
for PA 11/11/80  
dial

April 1980

80 4 11 022

SYNOPSIS

Chloro- and lithio-terminated diorganosilylene oligomers were coupled to form block copolymers that were soluble in common solvents and deposited coherent films from solution. Copolymer UV spectra showed a red shift in absorption maxima attributed to increased silicon chain length and phenyl-silicon spine interactions.

Accession For	
NTIS GRA&I	
DDC TAB	
Unannounced	
Justification <i>for file</i>	
By <i>[Signature]</i>	
Distribution/	
Availability Codes	
Dist	Avail and/or special
<i>A</i>	

## INTRODUCTION

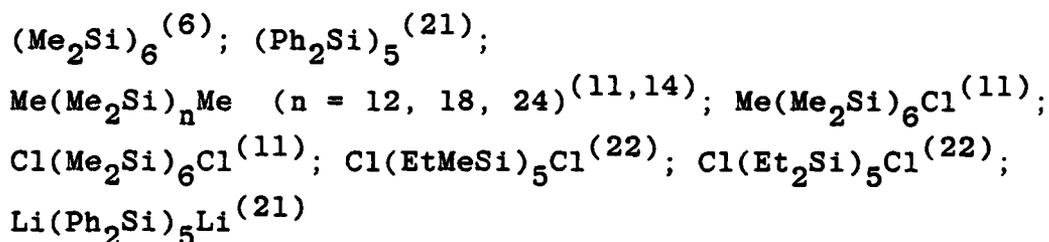
— Dimethylsilicon polymers of modest chain lengths (DP  $\sim$  55) were first described in 1949.<sup>(1)</sup> Thereafter, interest in organosilane high polymers lay dormant for a quarter century although study of cyclic and short chain organosilanes continued apace. Recently, two developments stimulated further interest in organosilane high polymers. Studies of low polymers had shown that electronic properties of homosilicon rings and chains resembled those of conjugated unsaturated carbon structures and suggested that such properties might develop more strongly in longer silicon chains.<sup>(2-15)</sup> In a quite different direction, it was reported that organosilane polymers could be pyrolyzed to form useful refractory silicon carbide compositions.<sup>(16-18)</sup> In both of these lines of inquiry, tractable organosilane polymers that form coherent films and fibers are especially useful. Because there was no information on high molecular weight organosilane polymers, we have prepared and examined several diorganosilane homopolymers and copolymers.

— High molecular weight polydimethylsilylenes (DP  $\sim$  600) prepared from specially purified dimethyldichlorosilane monomer were described in the first paper of this series.<sup>(19)</sup> These crystalline, high melting polymers were soluble only above 200°C and had no useful film forming qualities. A second paper described random copolymers of dimethylsilylene with dialkylsilylenes bearing ethyl and n-propyl groups.<sup>(20)</sup> Random copolymers containing small amounts of ethyl or n-propyl groups displayed substantially reduced solubilization temperatures but did not form coherent films. This third report describes some readily soluble, film forming block copolymers that have dialkylsilylene blocks alternating with diphenylsilylene blocks.

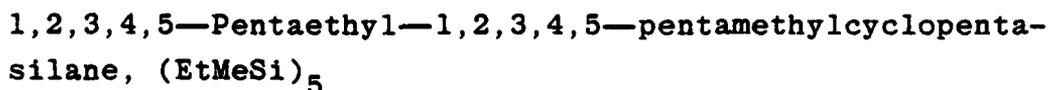
## EXPERIMENTAL

### Oligomers

Cyclic and linear oligomers listed below were prepared by methods based on published procedures:



Cyclic oligomers bearing ethyl groups —  $(\text{EtMeSi})_{5,6}$  and  $(\text{Et}_2\text{Si})_{5,6}$  — were made by methods similar to those cited above but required additional steps to separate side products contained SiH and SiO. These impurities were removed by conversion of SiH to SiOR and absorption of the polar alkoxy species on alumina. A typical procedure is described below.



Typically, dechlorination was run under dried nitrogen atmosphere in a flame dried 3l flask equipped with subatant thermometer, glass stirrer, addition funnel and large reflux condenser<sup>(20)</sup> in which 25g (1.09 mol) sodium, 85g (2.17 mol) potassium, 3g naphthalene and 650 ml tetrahydrofuran (THF) were stirred and heated until liquid alloy formed and dispersed and the dark color of naphthalide ion appeared. After cooling the mixture to 30C, 210 ml (1.51 mol) ethylmethyldichlorosilane were added dropwise over 4-5 hours at a rate that maintained 60C. The mixture was then held at 65C for 12 hours. To consume unreacted alloy, the mixture was cooled to 0C, stirred and treated by cautious dropwise addition of 10 ml acetic acid in 90 ml THF. After addition of

550 ml 10% aqueous acetic acid and 200 ml hexane, the upper organic layer was recovered, washed in sequence with 200 ml water, 200 ml 10% aqueous sodium bicarbonate and 200 ml water, then dried with anhydrous calcium sulfate, filtered and stripped of solvent. The crude product oil was a mixture of  $(\text{EtMeSi})_5$  and  $(\text{EtMeSi})_6$  along with some side products that contained SiH and SiO. To remove the side products, the crude was dissolved in 200 ml THF, 10 ml water and 330 mg chloroplatinic acid (in 2 ml dimethoxyethane) added, and stirred 2 hours. Ethanol, 20 ml, was then added dropwise (exotherm). The mixture was stripped of solvent, dissolved in 200 ml hexane and washed in sequence with 100 ml water, 100 ml 10% aqueous sodium bicarbonate, 100 ml water, dried with calcium sulfate and filtered. The solution was then passed through a column of neutral alumina (300g), eluted with 1600 ml hexane and solvent stripped to give 32.6g (30%) of oil which was a 65:35 mixture of  $(\text{EtMeSi})_5$  and  $(\text{EtMeSi})_6$ . Distillation of 46.0g of the mixed cyclosilanes through a 25 cm glass bead packed column gave 25.0g  $(\text{EtMeSi})_5$  (bp 118-130°C, 0.1 mmHg) at 98<sup>+</sup>% purity.

Decaethylcyclopentasilane,  $(\text{Et}_2\text{Si})_5$

$(\text{Et}_2\text{Si})_5$  (bp 190-200°C, 0.2 mmHg) was prepared in 99<sup>+</sup>% purity by the method given above for  $(\text{EtMeSi})_5$ .

### Copolymers

Copolymers were made both by adding a chloro-terminated oligomer in THF to a freshly prepared solution of  $\text{Li}(\text{Ph}_2\text{Si})_5\text{Li}$  and by addition in reverse order. To avoid decomposition of the sensitive  $\text{Li}(\text{Ph}_2\text{Si})_5\text{Li}$  reagent, the apparatus shown in Figure 1 (100 ml reaction chambers) was used. Typically, the apparatus was flame dried and kept with a slow stream of dry argon throughout reagent preparation and copolymer formation. For a reverse order

addition, 1.25g (2.5 mmol)  $\text{Cl}(\text{Et}_2\text{Si})_5\text{Cl}$  in 15 ml THF was placed in the lower chamber and in the upper chamber 2.28g (2.5 mmol)  $(\text{Ph}_2\text{Si})_5$  in 30 ml THF and 0.17g (25 mmol) lithium wire reacted at 35C for 4 hours to form  $\text{Li}(\text{Ph}_2\text{Si})_5\text{Li}$ . The solution of  $\text{Li}(\text{Ph}_2\text{Si})_5\text{Li}$  was then added dropwise in about 2.5 hours to the well stirred  $\text{Cl}(\text{Et}_2\text{Si})_5\text{Cl}$  so that the color imparted by each drop was fully discharged before the next was added. If any color persisted at the end, a drop or two of  $\text{Cl}(\text{Et}_2\text{Si})_5\text{Cl}$  solution was added. After stripping of THF, the crude polymer-salt mixture was taken up in 50 ml toluene and 50 ml ethyl ether, extracted with 50 ml water followed by 50 ml saturated aqueous NaCl, filtered through anhydrous calcium sulfate and stripped of solvent. The crude polymer in 5 ml toluene was added dropwise to 100 ml ethanol and the resulting precipitated polymer was filtered off and vacuum dried.

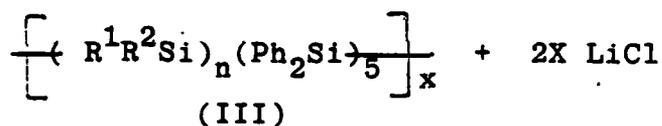
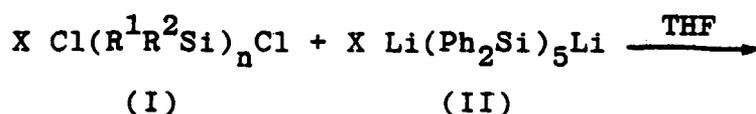
#### Analytical Methods

- IR Spectra: copolymers in KBr wafers; Digilab 10C Fourier Transform Spectrometer
- UV Spectra: copolymers in dimethoxyethane ( $17\text{-}36 \text{ mgL}^{-1}$ ); Beckman Model 25 Spectrometer
- NMR Spectra: copolymers in carbon tetrachloride (10-12 wt %); acetone internal reference (2.17 ppm, 130 Hz); Varian T-60 Spectrometer
- Molecular Weight:  $\bar{M}_n$ , copolymer in toluene ( $12\text{-}30 \text{ gL}^{-1}$ ) at 65C; Knauer Vapor Osmometer -  $\bar{M}_n$ , in toluene ( $1\text{-}10 \text{ gL}^{-1}$ ) at 25C; Chromatix KMX-6 LALLS Spectrometer.

Supplementary data for purity and structure of monomers and oligomers obtained by elemental analysis and GC-Mass Spectrometry.

## RESULTS AND DISCUSSION

Couplings of silyl lithium oligomers, such as  $\text{Li}(\text{Ph}_2\text{Si})_{4,5}\text{Li}$ , with monomeric chlorosilanes have been used successfully for preparation of several linear and cyclic silane oligomers of mixed organic substitutions. (21,23-25) The organosilane copolymers reported here were made by coupling  $\alpha,\omega$ -dichlorodialkylsilane oligomers (I) with 1,5-dilithio-decaphenylpentasilane (II):



	$\underline{\text{R}^1}$	$\underline{\text{R}^2}$	$\underline{n}$
(III-3)	Me	Me	6
(III-5)	Me	Et	5
(III-8)	Et	Et	5

In this scheme, the use of oligomer pairs capable of coupling only with each other was expected to favor alternating block structure in the copolymers (III) and avoid the formation of homopolymer side products that often complicates block copolymer preparations.

The coupling reactions were at first run by adding chloro oligomer dropwise to II until the red color of silyl lithium was just discharged. This procedure worked well for IIIa and gave a high polymer fraction with the expected proportions of alkyl and aryl H by NMR. However, the same procedure when used for IIIb and IIIc gave products with high alkyl H to aryl H ratios indicative of deficiencies of phenyl substituents. Significant amounts of  $(\text{Ph}_2\text{Si})_4$  were found in the product fraction remaining after high polymer precipitation which suggested that copolymer formed early or was undergoing re-arrangement catalyzed by as yet unreacted silyl lithium oligomer. Re-arrangements of various diphenylsilylene containing oligomers to form  $(\text{Ph}_2\text{Si})_4$  are known to be catalyzed by silyl lithium compounds. (21, 26-29) Increasing the rate of chlorosilane oligomer addition to decrease exposure time was not helpful but reversing the order of addition using the apparatus of Figure 1 gave copolymers with alkyl H to aryl H ratios closer to expected values as shown in Table 1.

Yields of precipitated copolymers ran 35-50% on starting oligomers and molecular weights ( $\bar{M}_n$ ) were about 5000-10,000. The copolymers were all very soluble in common solvents including tetrahydrofuran, diethyl ether, tetrachloromethane and toluene. In contrast to homopolymers and random copolymers examined earlier (19, 20) which had no useful film forming qualities, these block copolymers formed uniform coherent films by evaporation of solvent from solutions at room temperatures.

Infra-red spectra of the copolymers (Figure 2) and absorption assignments (Tables 2-4) are in agreement with the expected polymeric structures. (23, 30)

The UV spectra of the copolymers show strong absorptions in the 338-345 nm region (Table 5). Similar absorptions have been reported for several linear oligomers<sup>(14,31)</sup> (Table 6) and have been attributed to the silicon spinal chain acting as a  $\sigma$ - $\pi$  chromophore.<sup>(3,4,5)</sup> The shift of absorption maximum to longer wavelengths is probably related to increased chain length of the copolymers and increased conjugative interactions between phenyl substituents and the silicon spinal chain.

We are grateful to our colleagues C. L. Angell, C. S. Blackwell, D. V. Bowen, and I. R. Ladd for their advice and assistance. This work was supported in part by the Office of Naval Research.

## REFERENCES

- 1) C.A. Burkhard, J. Am. Chem. Soc., 71, 963 (1949);  
U.S. Patent 2,554,976 (1951)
- 2) M. Kumada and K. Tameo, Adv. Organomet. Chem., 6, 80 (1968)
- 3) H. Gilman, W.H. Atwell, F.K. Cartledge, Adv. Organomet. Chem., 4, 1 (1966)
- 4) K.M. MacKay and R. Watt, Organomet. Chem. Rev., 4, 137 (1969)
- 5) E. Hengge, Fortschr. Chem. Forsch., 51, 1 (1974)
- 6) E. Carberry and R. West, J. Am. Chem. Soc., 91, 5440 (1969)
- 7) G.R. Husk and R. West, J. Am. Chem. Soc., 87, 3993 (1965)
- 8) E. Carberry, G.E. Glass and R. West, J. Am. Chem. Soc., 91, 5446 (1969)
- 9) R. West, J. Polym. Sci., C, 29, 65 (1970)
- 10) V.F. Traven and R. West, J. Am. Chem. Soc., 95, 6824 (1973)
- 11) W.G. Boberski and A.L. Allred, J. Am. Chem. Soc., 96, 1244 (1974)
- 12) W.G. Boberski and A.L. Allred, J. Organomet. Chem., 71, C27 (1974)
- 13) W.G. Boberski and A.L. Allred, J. Organomet. Chem., 74, 205 (1974)
- 14) W.G. Boberski and A.L. Allred, J. Organomet. Chem., 88, 65 (1975)
- 15) W.G. Boberski and A.L. Allred, J. Organomet. Chem., 88, 73 (1975)
- 16) S. Yajima, J. Hayashi, M. Omori, Chem. Lett., Chem. Soc. Japan, 931 (1975)
- 17) S. Yajima, Ind. Eng. Chem., Prod. Res. Dev., 15 (3) 219 (1976)
- 18) S. Yajima, T. Shishido, K. Okamura, Ceram. Bull., 56 (12) 1060 (1977)

- 19) J.P. Wesson and T.C. Williams, J. Polym. Sci., Polym. Chem. Edn., 17, 2833 (1979)
- 20) J.P. Wesson and T.C. Williams, J. Polym. Sci., in press
- 21) H. Gilman and G.L. Schwebke, J. Am. Chem. Soc., 86, 2693 (1964)
- 22) H. Gilman and S. Inoue, J. Org. Chem., 29, 3418 (1964)
- 23) E. Hengge and D. Wolfer, J. Organomet. Chem., 66, 413 (1974)
- 24) E. Hengge and G. Kollman, J. Organomet. Chem., 92, C43 (1975)
- 25) H.J.S. Winkler, A.W.P. Jarvie, D.J. Peterson and H. Gilman, J. Am. Chem. Soc., 83, 4089 (1961)
- 26) H. Gilman and G.L. Schwebke, J. Organomet. Chem., 3, 382 (1965)
- 27) A.W.P. Jarvie and H. Gilman, J. Org. Chem., 26, 1999 (1961)
- 28) H. Gilman, D.J. Peterson, A.W. Jarvie and H.J.S. Winkler, Tetrahed. Lett., 5 (1960)
- 29) S. Kumada, M. Ishakowa, S. Sakamoto and S. Maeda, J. Organomet. Chem., 17, 223 (1969)
- 30) U.G. Stolberg and H.P. Fritz, Z. anorg. allgem. Chem., 330, 1 (1964)
- 31) H. Gilman, W.H. Atwell and G.L. Schwebke, J. Organomet. Chem., 2, 369 (1964)

Table 1	Effect of Order of Addition on Copolymer Composition
Table 2	Infra-Red Absorptions: Copolymer III-3
Table 3	Infra-Red Absorptions: Copolymer III-5
Table 4	Infra-Red Absorptions: Copolymer III-8
Table 5	Ultra-Violet Absorptions of Copolymers
Table 6	Ultra-Violet Absorptions of Oligomers

Figure 1            Copolymerization Reactor

Figure 2            Infra-Red Spectra of Copolymers

TABLE 1  
EFFECT OF ORDER OF ADDITION ON  
COPOLYMER COMPOSITION

<u>Copolymer</u>	<u>Method</u> <sup>(1)</sup>	<u>Alkyl H/Aryl H</u> <sup>(2)</sup>	
		<u>Calculated</u>	<u>Found</u>
III-3	A	0.72	0.73
	B	0.72	0.73
III-5	A	0.80	0.85
	B	0.80	0.80
III-8	A	1.0	1.4
	B	1.0	1.1

- (1) A: Chloro-oligomer added to lithio-oligomer.  
 B: Lithio-oligomer added to chloro-oligomer.

- (2) By H<sup>1</sup>-NMR

TABLE 2

INFRA-RED ABSORPTIONS: COPOLYMER III-3

<u>Wavenumber, cm<sup>-1</sup></u>	<u>Assignments (23,30)</u>
(3430)	(H <sub>2</sub> O Stretch)
3065, 3055, 3010, 2995, 2960, 2895	CH Stretch
1955, 1890, 1820, 1770	Phenyl
(1630)	(H <sub>2</sub> O Overtone)
1480, 1425	Phenyl
1400	CH <sub>3</sub> Deformation
1245	CH <sub>3</sub> Bending
1090, 1065(s), 1025, 995	Phenyl
835, 765	(CH <sub>3</sub> ) <sub>2</sub> Si Rocking
730	Phenyl
659, 630	Si-C Stretch
470, 425	Si-Si

(s): Shoulder

TABLE 3

INFRA-RED ABSORPTIONS: COPOLYMER III-5

<u>Wavenumber, cm<sup>-1</sup></u>	<u>Assignments (23, 30)</u>
(3450)	(H <sub>2</sub> O Stretch)
3065, 3055, 3010, 2995 2960, 2930, 2895, 2865	CH Stretch
1955, 1890, 1820, 1770	Phenyl
(1640)	(H <sub>2</sub> O Overtone)
1485	Phenyl
1455	CH <sub>3</sub> (C) Deformation
1425	CH <sub>3</sub> (Si) Deformation
1375	CH <sub>3</sub> (C) Bending
1245	CH <sub>3</sub> (Si) Bending
1090, 1065(s), 1030	Phenyl
1005	CH <sub>3</sub> CH <sub>2</sub> Si
785(s)	Phenyl
755	(CH <sub>3</sub> ) <sub>2</sub> Si Rocking
730	Phenyl
680(s)	SiC Stretch
470, 425	Si-Si

(s): Shoulder

TABLE 4

INFRA-RED ABSORPTIONS: COPOLYMER III-8

<u>Wavenumber, cm<sup>-1</sup></u>	<u>Assignments (23, 30)</u>
(3440)	(H <sub>2</sub> O Stretch)
3065, 3055, 3010, 2995, 2960, 2930, 2895, 2860	CH Stretch
1955, 1890, 1820, 1770	Phenyl
(1635)	(H <sub>2</sub> O Overtone)
1485	Phenyl
1455(s)	CH <sub>3</sub> (C) Deformation
1425	CH <sub>3</sub> (Si) Deformation.
1375	CH <sub>3</sub> (C) Bending
1235	CH <sub>3</sub> (Si) Bending
1090, 1070(s), 1030(s)	Phenyl
1000	CH <sub>3</sub> CH <sub>2</sub> Si
855, 765(s)	(CH <sub>3</sub> ) <sub>2</sub> Si Rocking
795, 735(s)	Phenyl
620	Si-C Stretch
475, 420	Si-Si

(s): Shoulder

TABLE 5  
ULTRA-VIOLET ABSORPTIONS OF COPOLYMERS

<u>Copolymer</u>	<u>Wavelength, nm</u>	<u>Absorptivity, cm<sup>2</sup>g<sup>-1</sup></u>
III-3	338	46,700
	270(s)	-----
	230	42,800
III-5	345	53,500
	281(s)	-----
	269(s)	-----
	262(s)	-----
	220(s)	-----
III-8	342	34,000
	269(s)	-----
	262(s)	-----
	220(s)	-----

(s): Shoulder

TABLE 6  
ULTRA-VIOLET ABSORPTIONS OF OLIGOMERS

<u>Oligomer</u> <sup>(1)</sup>	<u>Wavelength (max.), nm</u>	<u>Absorptivity, cm<sup>2</sup>g<sup>-1</sup></u>	
Me <sub>3</sub> Si(Ph <sub>2</sub> Si) <sub>5</sub> - SiMe <sub>3</sub>	309	31,900	
	268(s)	-----	
	220(s)	-----	
	229	46,800	
Ph(Ph <sub>2</sub> Si) <sub>7</sub> Ph	323	29,300	
	269(s)	-----	
	262(s)	-----	
	231	51,900	
Me(Me <sub>2</sub> Si) <sub>n</sub> Me	n = 12	286	44,500
		241(s)	-----
		230(s)	-----
	n = 18	292	51,300
		233(s)	-----
	n = 24 <sup>(2)</sup>	294	33,700
220		34,000	

(s): Shoulder

(1): In dimethoxyethane

(2): In tetrahydrofuran



FIGURE 2: INFRA-RED SPECTRA OF COPOLYMERS

