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Silicon and Carbon Solid-State MAS and Liquid-State NMR Study of the Polycondensation of Heteropolysiloxanes

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Discussion

The results presented here lead us to conclude that the periodate-Mn(II) oscillator and the permanganate-reductant oscillators form two branches of a single family of manganese-based oscillatory reactions and that elucidation of the mechanism of one branch will contribute greatly to understanding how the other branch works. In both types of reaction, the major end product is Mn(IV), which accelerates its own production. A full description of these reactions requires all oxidation states of manganese from +2 to +7. The contribution of each state to any particular oscillator will depend upon both the pH and whether the partner of the manganese species is a one- or a two-electron reagent.

There do, however, appear to be essential differences between the two types of oscillator. The permanganate-reductant systems^{2,3,7} require an auxiliary third component, H_2PO_4^- or HPO_4^{2-} , which is not necessary for the Mn(II)-oxidant reaction. These stabilizing species slow down, regulate, or prevent the flocculation of Mn(IV) species to solid MnO_2 . The MnO_4^- oscillators do not exhibit the pH oscillation found in the Mn(II)-periodate system.

It is possible that these differences are not so fundamental as they might seem. We have shown that addition of phosphate does broaden the range of oscillation of the present system. We note that in one recently characterized permanganate oscillator,⁸ only two components are necessary, arsenite and permanganate. The arsenate product serves in place of phosphate as the stabilizer for Mn(IV). We suggest that periodate plays an analogous dual role, serving as both oxidant and stabilizer. In support of this view, we offer three pieces of evidence. First, the broad yellow band in the absorption spectrum of the reacted mixture shifts toward lower wavelengths as $[\text{IO}_4^-]$ is increased. Second, Jensovsky²⁰

reports that orthoperiodate can stabilize such anomalous oxidation states as Mn(IV), Co(III), Cu(III), and Ag(III) by complex formation. Finally, Lister et al.^{21,22} have prepared and characterized Mn(IV)-periodate complexes by oxidizing MnSO_4 with $\text{Na}_2\text{H}_3\text{IO}_6$.

The permanganate oscillators oscillate in buffer and show negligible pH oscillations, perhaps because of the buffering ability of the added phosphate. They are clearly not pH oscillators. The Mn(II)-periodate system in contrast shows measurable oscillations in pH, and buffering strongly suppresses or eliminates the oscillations in Pt potential and absorbance. This system thus meets the criteria for a pH oscillator.²³ However, the amplitude of the pH oscillation is significantly smaller than that of other pH oscillators, and a small Pt potential oscillation does persist even with buffering. Thus the characterization of the $\text{Mn}^{\text{II}}\text{-IO}_4^-$ system as a pH oscillator is marginal.

The simulations presented in Figures 5 and 6 are in good qualitative agreement with experiment. They suggest that we are on the right track. However, none of the rate constants used in those calculations has been measured; all were estimated. We hope that the results presented here, together with the likelihood that understanding this system will lead to further insights into permanganate oscillators and into manganese chemistry of considerable practical importance, will soon lead to further study of the kinetics of the component reactions.

Acknowledgment. We thank Kenneth Kustin for helpful discussions. This work was supported by the National Science Foundation and by a U.S.-Hungarian Cooperative Grant from the NSF and the Hungarian Academy of Sciences.

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Silicon and Carbon Solid-State MAS and Liquid-State NMR Study of the Polycondensation of Heteropolysiloxanes

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Abstract: Samples were taken at various stages of the polycondensation between different silicon alkoxides $\text{RSi}(\text{OR}')_3$, which are reacted together in the preparation of membranes for ultrafiltration and reverse osmosis. ^{29}Si NMR spectra could be interpreted by using empirical increments of the chemical shift, which are characterized for substitutions at the Si atom. It is found that the reaction attains the maximum degree of condensation forming a three-dimensionally infinite siloxane $\text{RSi}(\text{OSi}\equiv)_3$ backbone, which is, however, partially degraded by thermal treatment (120 °C) leading to $\text{R}_2\text{Si}(\text{OSi}\equiv)_2$ and $\text{Si}(\text{OSi}\equiv)_4$ groups. The organic part is not affected during these reactions, and side reactions in the early stages of polymerization (e.g. ligand exchange with the solvent) were reversible.

Introduction

Heteropolysiloxanes (HPS) are creating a growing interest in chemistry because of their composite nature,^{1,2} made up of an inorganic backbone of siloxane bonds and organic chains which are chemically bound to the backbone and can be used to modify

the material properties within a wide range. The early approach was to deposit these compounds on a porous ceramic support in order to obtain a quite dense membrane capable of performing liquid or gas separation. Several requirements must be met by such membranes:^{3,4} a few micrometers thickness, absence of

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[§] Instituto de Ciencia de Materiales CSIC.

(1) Schmidt, H. J. *Non-Cryst. Soln.* 1985, 73, 681-691.

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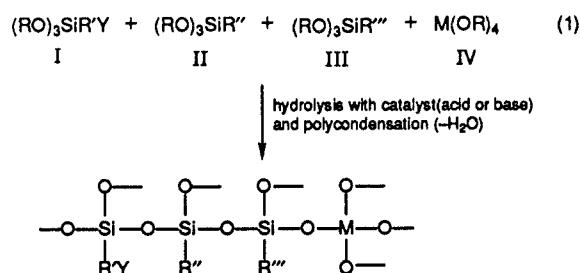
(4) Lonsdale, H. K. *NATO ASI SER., Ser. C, Synth. Membr. Sci. Eng. Appl.* 1986, 181, 155-186.

cracks, thorough adhesion at the interface between polymer and ceramic support, thermal and chemical resistance, and incorporation of suitable organic functions to ensure wettability, i.e. hydrophilic groups for use in an aqueous medium.

The present study is concerned with the synthesis of HPS using a sol-gel procedure and alkoxy silanes as starting materials.⁵⁻⁹ This method is very flexible and allows the combination of different monomer precursors during the various steps of hydrolysis and polymerization, so that, in principle, a great variety of specific organic functions can be introduced into the network in order to achieve the desired material properties. The correct evolution of the polymer is, however, not easy to prove because of its amorphous structure, and a great number of side reactions or simple physical mixtures could a priori not be excluded. A ²⁹Si and ¹³C NMR study has therefore been undertaken in order to determine the structure of the products at various stages of the polycondensation reaction and to confirm, in particular, the mixed organic-inorganic nature of the final polymer.

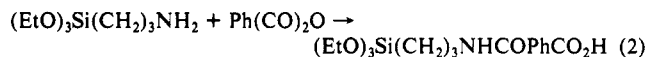
Experimental Section

Reaction Scheme for Sample Preparation. Several commercially available alkoxy silanes (Fluka Chemical Corp.) were combined in order to prepare a hydrophilic HPS which contains simultaneously different functional groups. The scheme of the complete reaction is



All four alkoxides (I, II, III, IV) are network-forming compounds. In addition, alkoxide I contains an organic hydrophilic function represented by Y. The role of each group of reactants is as follows:

(a) Group I is actually a couple of reactants which supply the hydrophilic function in the polymer. For the present study, we chose the amide function, -NH-CO-, obtained by reaction of 3-APS ((3-amino-propyl)triethoxysilane) with PAN (phthalic anhydride) (reaction 2). In



some cases, PAN was substituted by PYDAN (pyromellitic dianhydride).

(b) Group II is an alkoxy silane which takes part in the formation of the siloxane network and is able to perform a supplementary cross-linking through its organic part: 3-MPS ((3-methacryloxypropyl)trimethoxy-silane, $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OCOC}(\text{CH}_3)=\text{CH}_2$).

(c) Group III is a simple alkoxy silane, in order to complete the siloxane backbone and to warrant silicone-like surface properties to the final material: MTMS (methyltrimethoxy silane, $(\text{CH}_3\text{O})_3\text{SiCH}_3$).

(d) Group IV is a metal alkoxide M(OR)_4 which provides the polymer a higher mechanical resistance, a higher thermal stability, and especially good behavior during the gelation and drying steps:¹⁻⁶ TIPOT (tetra-isopropylorthotitanate, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$).

General Procedure. The starting materials were mixed in an organic medium (chloroform or ethanol distilled and stored on 4-Å molecular sieves). A typical composition for the initial alkoxy silane mixture was the following (wt % in the solvent): PAN or PYDAN 8-15, 3-APS 20-50, 3-MPS 10-25, MTMS 0-10, TIPOT 1-3. The reaction procedure can be divided into four main steps: (a) reaction between monomeric PAN and 3-APS in order to form the amide function -NH-CO-, i.e. the active part of the polymer (This step is performed in EtOH or CHCl_3 solution, at room temperature, or under reflux in CHCl_3 at 50-80 °C over 3-7 h.); (b) addition of the alkoxides of groups II, III and IV (i.e. 3-MPS, MTMS, TIPOT) (Polycondensation takes then place in the

Table I. Weight Percentages and Experimental Parameters of Step a for Samples Subjected to Reaction Steps a, c, and d

sample	PAN	PYDAN	3-APS	k	solvent CHCl_3	temp/ duration
1	14		31	1.5	55	room/7 h
2	13		47	2.5	40	room/7 h
3	14		31	1.5	55	50 °C/3 h
4	14		32	1.5	54	80 °C/7 h
5		11	32	3	57	room/7 h

mixture to create the inorganic network. During this step, the viscosity increases gradually according to the experimental conditions (temperature, solvent nature, concentrations, aging time); (c) aging over a few days at room temperature, which leads to a monolithic gel without visible shrinkage or crack formation; and (d) thermal treatment at 120-150 °C over 1-2 h which completes the gel dehydration and the drying step.

Reaction Parameters. In steps a and b, the following experimental parameters have been varied: molar ratio $k = 3\text{-APS/PAN}$; the nature of the anhydride (PAN or PYDAN); the temperature of the reaction; the nature of the solvent; the duration of reflux; and the addition of catalyst (HCl).

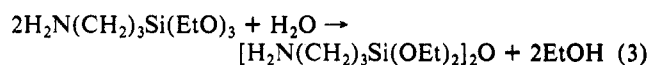
Aging for a few days and thermal treatment (1 h at 120 °C) were the same for all samples. Once dried, the gels were crushed in a ball mill and tightly compacted for structural characterization by solid-state NMR. In order to have a better insight into the structural evolution of the materials as a function of the above parameters, in some samples (1-5), step b has been omitted, whereas in other samples (6-13) the whole sequence of treatments from step a to step b was applied. Reaction parameters for the different samples are reported in Tables I and II.

Structural Characterization. Both liquid-state NMR spectroscopy and high-resolution MAS solid-state NMR spectroscopy were used. Liquid-state ²⁹Si and ¹³C NMR spectra were obtained on a BRUKER AC 250 MHz spectrometer at 49.7 and 62.9 MHz, respectively, in CDCl_3 at room temperature. MAS solid-state ²⁹Si and ¹³C spectra were recorded at room temperature with a BRUKER MSL 400 MHz spectrometer at 79.5 and 100.3 MHz, respectively. ²⁹Si spectra were obtained with use of the single pulse program CYCLOPS and the following parameters: $\pi/2$ -pulse time 5 μs and recycle time 5 s. ¹³C spectra were recorded with use of the CP-MAS program version which eliminates spinning side bands (TOSS), using the following parameters: $\pi/2$ -pulse time 5 μs , contact time 2 ms, decoupling time 25 ms, and recycle time 5 s. In all ¹³C spectra, the Hartmann-Hann condition was satisfied. TMS was used as external standard for ²⁹Si and ¹³C signals. The spinning frequency for solid samples was in the range of 4-5 kHz.

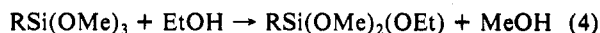
Results and Discussion

²⁹Si NMR Spectra: Central Part (-39 to -68 ppm). ²⁹Si NMR spectra were obtained for each of the solid-state samples in Tables I and II, as well as for the starting materials and several intermediate products in the liquid state. Some typical spectra are represented in Figures 1 and 2, showing that peaks occur in three distinct ranges with respect to the following chemical shifts: at -13 to -25, -39 to -68, and -100 to -120 ppm. A synoptic presentation of ²⁹Si NMR results for the central part of the spectra (-39 to -68 ppm) is given in Table III. It shows several possible compounds, i.e. Si environments which are formed during the polymerization, followed by expected and observed values for the chemical shift. Expected chemical shifts were calculated assuming that each substitution at Si is associated with a specific increment for its chemical shift. The increments have been evaluated from published data¹²⁻²³ and will be detailed in the next paragraph.

For the early stages of reaction, products were liquid and peak assignments are relatively straightforward. Thus, aged 3-APS in EtOH exhibits, in addition to the peaks of original 3-APS at -46 ppm, a peak at -52.8 ppm (Table III), which can be assigned to a dimeric molecule issued from reaction 3



i.e. the first step of the whole condensation process outlined in reaction 1. Similarly, aged solutions of 3-MSP and MTMS showed additional peaks at -44.5 and -40 ppm, respectively, which can be assigned (Table III) to the products of ligand exchange according to eq 4. Such exchange reactions are typical for



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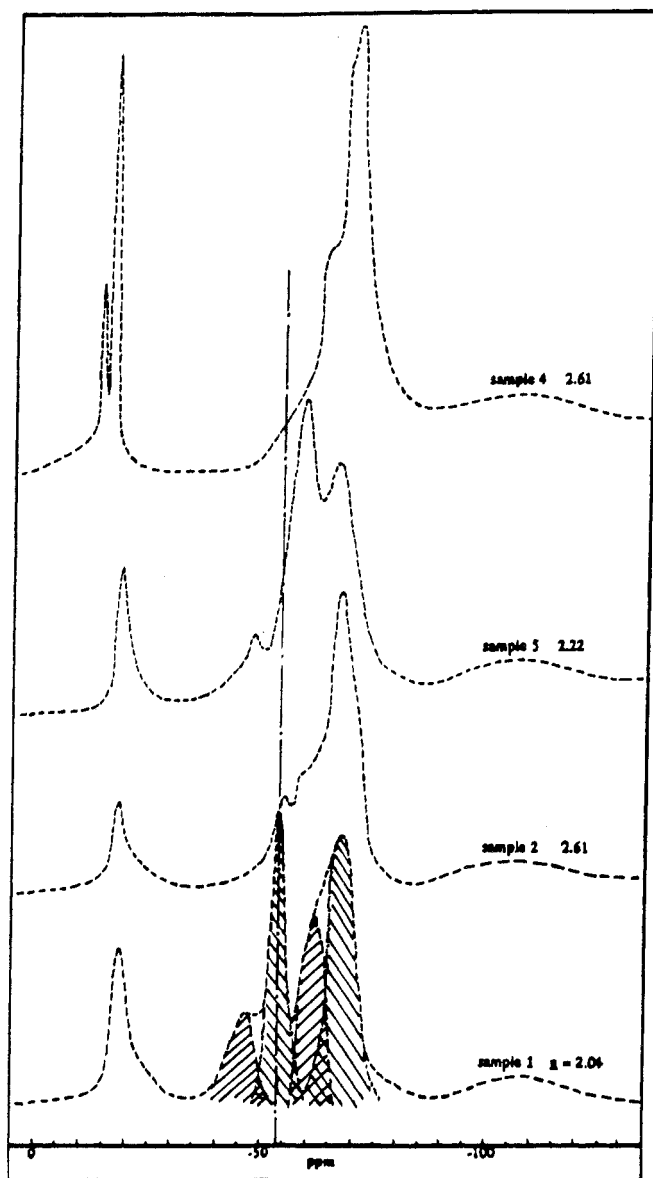
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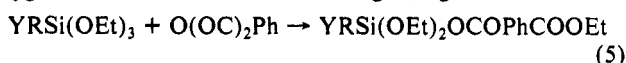
Table II. Weight Percentages and Experimental Parameters for Samples Subjected to the Full Sequence of Reaction Steps a–d^a

sample	PAN	3-APS	3-MPS	MTMS	TIPOT	solvent		temp/ duration of step a
						CHCl ₃	EtOH	
6	12	26	14		3	45		room/7 h
7	12	26	14		3	45		80 °C/3 h
8	11	27	14		3	45		80 °C/7 h
9	11	27	14		3	45 + HCl		80 °C/7 h
10	8	19	19.5		1.5	26	26	room/7 h
11	10	24	13.5	10	1.5		41	room/7 h
12	10	25	23				42	room/7 h
13	10	24	14	10			42	room/7 h

^a Molar ratio $k = 1.5$ for all samples. Catalyst (HCl) only for sample 9. Sample 10 has been prepared in CHCl₃ for step a and then in EtOH for the others steps.

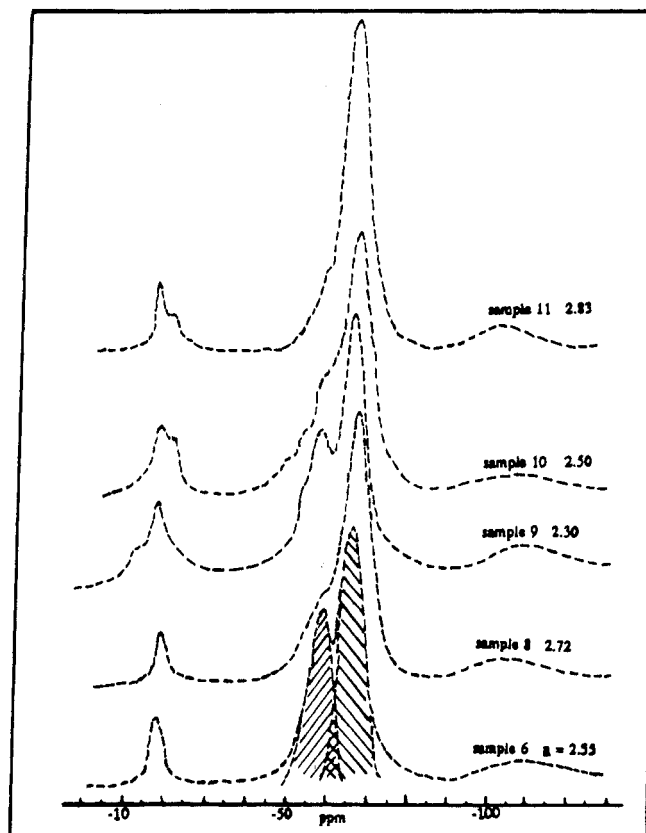
**Figure 1.** ²⁹Si NMR spectra of samples from Table I (n gives the average condensation degree of polymer backbone).

alkoxide solutions in nonhomologous alcohols.¹⁰ Another possible side reaction^{10,11} is attack by the anhydride (PAN) on the alkoxide oxygen instead of the end-chain nitrogen, e.g.



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**Figure 2.** ²⁹Si NMR spectra of samples from Table II (n has the same meaning as in Figure 1).

The corresponding peak is expected at -53.5 ppm and has been observed for a mixture of 3-APS and PAN in CHCl₃.

Once the products are solid, assignment is more difficult because of the elevated number of coexisting constituents and generally broader peaks in the solid-state NMR spectra. Nevertheless, it is well-established for silicate structures that progressive condensation is reflected in a constant increment of -10 ppm for each SiOH to SiOSi substitution at a given tetrahedral Si atom. This observation has successfully been used, for example, by Lippmaa et al.¹² to distinguish between different silica species in the series isolated tetrahedron–dimer–chain–sheet–three-dimensional framework. In a similar way, the condensation reaction of heteropolysiloxanes can be recognized from a constant increment of 6 to 7 ppm (toward higher field) for each SiOR to SiOSi substitution. An increment of 3 to 4 ppm toward lower field is typical for each SiOR to SiOH substitution and 3 to 5 ppm toward higher field for each SiOEt to SiOMe substitution.^{13,23}

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Table III. Different Species Occurring during Polycondensation Reaction 1 and Their Chemical Shifts in ^{29}Si NMR Spectroscopy^a

species	from reaction	expected shift, ppm	obsd shift, ppm	in samples (nos. refer to Tables I and II)
<u>$\text{R}=\text{NCH}_2\text{CH}_2\text{CH}_2\text{-}$</u> <u>$\text{RSi}(\text{OEt})_3$</u>		<u>-46^a</u>	<u>-46^a</u>	<u>original 3-APS, liq</u>
$\text{RSi}(\text{OEt})_2(\text{O-})^b$	3	-53	-46.3 -52.8 -53.7; -54.8	1, 3 aged 3APS in EtOH 1, 2, 3
$\text{RSi}(\text{OEt})(\text{O-})_2$	1	-60	-58.6 to -61	1, 2, 3, 4, 5, 6, 7, 8, 9, 10
$\text{RSi}(\text{O-})_3$	1	-67	-66 to -67.5; -64.5 to -67.7	1, 2, 3, 4, 5, (6), 7, 8, 9, 10, 11
$\text{RSi}(\text{OEt})_2(\text{O-PAN})$	5	-53.5 liq obs	-53.5; -53.5 to 54.8	3APS/PAN in CHCl_3 liq; 1, 2
$\text{RSi}(\text{OEt})(\text{OH})(\text{O-})$	hydrolysis	-49 theor calc	-48; -49.6; -50.6	5, 7, 10
<u>$\text{R}=\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$</u> <u>$\text{RSi}(\text{OMe})_3$</u>		<u>-42.4^a</u>	<u>-42.4^a</u>	<u>original 3-MPS, liq</u>
$\text{RSi}(\text{OMe})_2(\text{O-})$	3	-49	-49; -50.6	7, 10
$\text{RSi}(\text{OMe})(\text{O-})_2$	1	-55	-54.5 to -55	9, 10
$\text{RSi}(\text{O-})_3$	1	-61	-60.3 to -60.6	7, 11
$\text{RSi}(\text{OMe})_2(\text{OEt})$	4 (side reaction)	-44.5	-44.5	aged 3-MPS in EtOH, liq
<u>$\text{R}=\text{CH}_3$</u> <u>$\text{RSi}(\text{OMe})_3$</u>		<u>-39^a</u>	<u>-39^a</u>	<u>original MTMS, liq</u>
$\text{RSi}(\text{OMe})_2(\text{OEt})$	4 (side reaction)	-40	-40	aged MTMS in EtOH, liq

^a Underlined entries are used as references for the calculation of expected shifts below. ^b O- stands for an -O-Si= bridge.

Thus, the SiOSi bridge formation in samples 1 to 5 (Figure 1 and Table III) is reflected by a decrease in intensity of the monomer 3-APS peak at -46.3 ppm and the appearance of peaks at -53, -60, and -67 ppm. In sample 1 (Figure 1), an abnormally high and narrow peak at -53.7 ppm is observed. This peak should be due, to a great extent, to the product of the side reaction with PAN (eq 5) which might be kinetically favored in the early stages of reaction. Support for this hypothesis comes also from sample 2 (Figure 1), where the peak at -53.7 ppm is much smaller according to a lower proportion of PAN in the batch composition, as well as from comparison of samples 1-4, where higher temperature and longer reaction time for step a are seen to favor condensation to the detriment of the side reaction 5.

The starting 3-APS monomer has three Si-OEt bonds suggesting that the final polymer might have a three-dimensional siloxane backbone. In order to prove this, an average condensation degree of Si tetrahedra in the different polymer samples has been calculated by using eq 6

$$n = \sum_{n=0}^3 nI_n \quad (6)$$

where I_n is the relative intensity peaks corresponding to Si in $\text{RSi}(\text{OR})_{3-n}(\text{OSi=})_n$ environments. I_n was obtained from deconvolution of the experimental spectra in terms of elementary peaks of gaussian shape (see samples 1 and 6 in Figures 1 and 2). The average condensation degree n is given as a parameter in Figures 1 and 2 and is seen to vary between 2.0 (for sample 1) and 2.83 (for sample 11). This means that the silicate backbone of the fully condensed polymer is, as expected, almost three-dimensionally infinite. The actually achieved condensation degree depends, however, on various factors. Thus, comparison of samples 1-6-10-11 (Figures 1 and 2) suggests that a full condensation is more easily attained in EtOH than CHCl_3 as solvent, and comparison of samples 4-5 (Figure 1) shows that the replacement of PAN by PYDAN favors the product where only two OR functions are substituted by OSi bridges, i.e. full condensation seems to be hindered by the bifunctional and rigid PYDAN molecule.

Another case with strong peaks and shoulders at lower field is sample 9 as compared with sample 8 (Figure 2): evidently, and in agreement with other authors,^{1,7-9} the catalytic effect of HCl favors hydrolysis with respect to the condensation reaction. Therefore, Si-OH and Si-OR are equivalent with respect to condensation degree and we cannot give further conclusion about it. Polymers containing 3-MPS and MTMS are not discussed because of the starting mixture complexity.

^{29}Si NMR Spectra: Outer Ranges (-100 to -120 ppm and -13 to -25 ppm). Peaks in these ranges have not been expected for the present study. The broad peak at -100 to -120 ppm (Figures

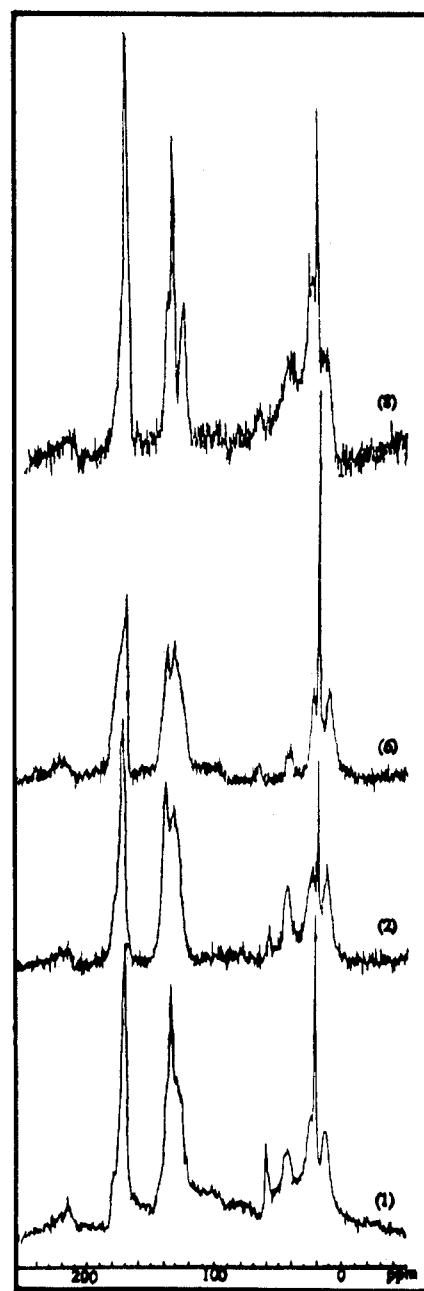
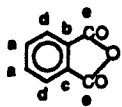


Figure 3. ^{13}C NMR spectra of some representative samples.

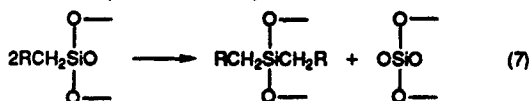
Table IV. ^{13}C NMR Chemical Shifts for Initial Alkoxides in the Liquid State and HPS Polymers in the Solid State*

alkoxide and chemical groups	chemical shifts, ppm	
	in the liquid state in CDCl_3	in the solid state
3-APS $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{Si}-(\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4)_3$	a 7.8 b 18.4 c 27.4 d 45 e 58.4	12 to 13 20.4 23.8 to 25.2 41.8 to 46.9 59.3 to 59.8 ethanol 44 to 45.2 alkoxide
PAN  amide or imide $\text{NC}=\text{O}$ with steric hindrance	a 126.5 b 132.46 c 132.55 d 137.43 e 164.4	125.8 to 131 133.4 to 137 169.7 to 172.2 170 to 178 212.7 to 215
3-MPS $\text{H}_2\text{C}=\text{C}_6(\text{C}_6\text{H}_5)-\text{C}_6(\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{Si}(\text{O}-\text{C}_6\text{H}_4)_3$	a 5.6 b 18.3 c 22.4 d 50.5 e 66.7 f 125 g 137 h 167.4	12 to 14.5 20.1 26.8 to 27.3 not observed 66.8 to 67.4 125.4 to 125.6 137.8 to 138.6 170
MTMS $\text{C}_6\text{H}_5-\text{Si}-(\text{OC}_6\text{H}_5)_3$	a -8.8 b 50.4	not observed
TIPOT $\text{Ti}(\text{OC}_6\text{H}_4(\text{C}_6\text{H}_5)_2)_4$	a 26.6 b 76.6	not observed

* Assignments in the liquid state are experimental data.

1 and 2) can be assigned to Si bound to four OSi groups, a configuration well-known from silica and many framework silicates.^{13,16-18} Peaks at about -20 ppm, on the other hand, have been reported^{13,15,16,17,24} for Si bound to two OSi plus two CH_2R groups.

Peaks always appear in both outer ranges together, suggesting that a ligand exchange (reaction 7) takes place during the final thermal treatment (1 h at 120 °C).



This is a well-known reaction in silicone chemistry, but it implies cleavage of Si-O and Si-C bonds and its occurrence under the relatively mild conditions of the present study is surprising.^{26,27} Although undesirable for the definition of the HPS polymer, this observation is, however, of much interest for the chemistry of silicon. A forthcoming study will therefore be dedicated to this subject.

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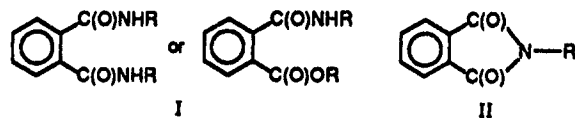
^{13}C NMR Spectra. ^{13}C NMR spectra have been obtained for each of the liquid starting materials, as well as for several significant samples among the solid polymers (samples 1, 2, 4, 6, 7, 8 in Tables I and II). Results are summarized in Table IV, which shows the distinct possible carbon environments followed by the corresponding chemical shifts in the liquid (column 2) and the solid state (column 3). Some representative spectra for solid samples (1, 2, 6, 8) are represented in Figure 3.

For the present study, only the comparison of liquid- and solid-state spectra have been considered in order to get information about the polycondensation mechanism. One important observation is that each carbon environment of the solid samples has its counter part in the liquid samples. This means that no "organic" reaction occurs during the polycondensation and the thermal treatment, i.e. the carbon chains are kept unaltered. Further important observations are the following:

(a) Peak broadening and a slight shift toward lower fields (e.g. from 6/8 to 12/14 ppm for CH_2Si groups, Table IV) are typical for compounds with a high condensation degree, confirming that the organic chains participate in the polymer.

(b) Peaks assigned to SiOR groups in the liquid state (18.4 and 58.4 ppm for 3-APS and 50.5 ppm for 3-MPS, Table IV) decrease (samples 1, 2, 4) or vanish (sample 6, 7, 8) when passing to the solid samples. This is in support of a full condensation which eliminates SiOR groups.

(c) In the range of carbonyl $\text{C}=\text{O}$ (about 170 ppm), a double peak or shoulder is generally observed. Since the splitting is more pronounced for the composition with higher 3-APS content (sample 2), the doublet (170 and 178 ppm) is thought to be due to a high content of configurations (I), whereas the peak at 170 ppm (typical for lower k and higher temperature) might be associated with the imide configuration (II):



These peaks are coupled with a broad, weak resonance at 215 ppm which is characteristic for sterically restrained carbonyl groups,

consistent with a high condensation degree of the samples.

(d) Peaks corresponding to the alkene C atoms in 3-MPS are retained in the polymer samples (Table IV), which suggests that vinylic polymerization did not take place under the conditions of the present study. In fact, no NMR observation allows us to conclude on this reaction.

Conclusions

The aim of this work was to prepare specific materials usable in membrane technologies. As illustrated in this paper, a large variety of molecular precursors can be combined in order to prepare tailored organic-inorganic polymers such as heteropolysiloxanes.

An NMR investigation showed that condensation of heteropolysiloxanes from alkoxy silanes can be successfully completed providing that reaction conditions are adaptable to the different precursors.

From a chemical point of view, some important conclusions can be drawn for the preparation of these heteropolysiloxanes: replacement of PAN by PYDAN stops the condensation at an

average condensation degree of about $n = 2.2$; full condensation ($n = 3$) is attained after a 7 h reaction time for the first step; high temperature (80 °C) and EtOH as solvent instead of CHCl_3 favor full condensation (In the early stages, however, EtOH gives rise to side reactions. A change of solvent would therefore be the method of choice.); the thermal treatment at 120 °C partially degrades the polymer backbone and should therefore be replaced by an alternative curing procedure.

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Registry No. (3-APS)(PAN) (copolymer), 131618-03-6; (3-APS)-(PYDAN) (copolymer), 131618-04-7; (3-APS)(PAN)(3-MPS)(TIPOT) (copolymer), 131618-05-8; (PAN)(3-APS)(3-MPS)(MTMS)(TIPOT) (copolymer), 131618-06-9; (PAN)(3-APS)(3-MPS) (copolymer), 131618-07-0; (PAN)(3-APS)(3-MPS)(MTMS) (copolymer), 131618-08-1.

Orientation and Dynamics of β -Dodecyl Glucopyranoside in Phospholipid Bilayers by Oriented Sample NMR and Order Matrix Analysis

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Abstract: The structure of the glycolipid analogue β -D-dodecyl glucopyranoside (BDOG) in a phospholipid bilayer environment is presented. Isotopically labeled BDOG was synthesized, solubilized in a magnetically orientable membrane system composed of 1,2-dimyristoyl-*sn*-3-glycerophosphocholine (DMPC) and 3-[(cholamidopropyl)dimethylammonio]-2-hydroxy-1-propanesulfonate (CHAPSO), and examined by an array of 1-D and 2-D NMR methods. This allowed measurement of two quadrupolar coupling constants for glucose ring deuterons, five ^{13}C - ^1H dipolar splittings, and six ^{13}C - ^{13}C dipolar splittings. Furthermore, manipulation of the sample to monotonically scale down the anisotropic part of the nuclear spin interactions permitted the absolute signs of most of the coupling constants to be determined. This set of data allowed analysis of the full order matrix for the system and subsequent determination of the average orientation of the glucose ring with respect to the bilayer normal. The results indicate that the glucose ring is extended from the plane of the bilayer with the vector between carbons 2 and 6 approximately parallel to the plane. Motions of the ring perpendicular to the normal are restricted in an anisotropic manner, apparently to avoid placing either the 2- or 6-substituents into apolar regions of the membrane. While the average orientation is similar to that obtained by assuming axial symmetry and a single order parameter, the complete analysis offers important insight into the degree and nature of motions executed at the surface of membranes.

The dynamics, three-dimensional structure, and orientation of the carbohydrate portions of membrane-associated glycoforms (glycolipids and glycoproteins) are matters of importance given the role these molecules play in cell surface recognition events such as the binding of toxins, lectins, antibodies, and other cells.¹ Characterization of their properties is also of importance in understanding how oligosaccharides are biosynthesized at the membrane surface,²⁻⁴ how the toxicity of bacterial lipopolysaccharides arises, and what role the glycosylphosphatidylinositol anchor plays in the association of many peripheral proteins with membrane surfaces.⁵

Structural studies of oligosaccharides that require chemical or enzymic cleavage to solubilize or facilitate crystallization of the oligosaccharide have contributed much to our current knowledge. X-ray crystal structures of complex saccharides are relatively rare, but data obtained for simple mono- and disaccharides⁶ provide important building blocks for further computational and experimental studies. High-resolution NMR has provided structures for somewhat larger molecules and some insight into allowed solution conformations.⁷⁻¹¹ The fundamental validity of the

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