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Redistribution Equilibria in Bromine-Terminated Poly(dimethylsilthians)

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Hexamethylcyclotrisilthian and dibromodimethylsilane upon heating form liquids which, by proton nuclear magnetic resonance spectroscopy, are shown to be mixtures of molecules. The equilibria resulting from exchange on the dimethylsilicon moiety of bridging sulfur atoms with bromine atoms are shifted strongly towards ring compounds. At equilibrium, measured at 150° and 200 °C, in addition to relatively small amounts of short chain molecules, two sizes of ring molecules are seen, with the trimer predominating over the dimer. The appropriate equilibrium constants giving the distribution of chain and ring molecules are presented and it is shown that these adequately describe the distribution of molecules at equilibrium.

Introduction

In an earlier study [1] from this laboratory we have presented evidence for the existence of equilibria between chain and ring molecules when dichlorodimethylsilane is equilibrated with hexamethylcyclotrisilthian. In these equilibria ring molecules were favored over chain molecules with the latter being present in relatively small amounts and being of short chain length. The present work was undertaken to study further the redistribution equilibria in halogen-terminated poly(dimethylsilthians) since in the earlier study [1], where the halogen was chlorine, the proton nmr signals of the dimethylsilicon groups in the various molecules at equilibrium were compressed into the narrow range of *ca.* 0.11 ppm. This feature prevented us from observing the fine structure seen previously in other related systems [2–4] at equilibrium. By selecting bromine as terminating group the range of nmr resonances of the methyl groups in the various molecules was extended to about 0.45 ppm thus revealing the expected fine structure. The present paper reports the experimental study, the detailed interpretation of these nmr spectra and the analysis of the distribution of molecules at equilibrium in this system and represents part of our study of equilibria in organometallic polymers.

Experimental

Materials

Dibromodimethylsilane [5] and hexamethyltrisilthian [6] were prepared according to literature methods.

Sample Preparation, Equilibrium and Data Acquisition

The samples were prepared by mixing in standard 5 mm o.d. nmr tubes under anhydrous conditions various proportions of $(CH_3)_2SiBr_2$ and $[(CH_3)_2SiS]_3$. The samples were equilibrated directly in the sealed nmr tubes by heating at the desired temperature for various lengths of time until the nmr pattern did not change upon further heating. The data obtained at 150 °C correspond to a heating time of 7 days with all samples having reached equilibrium in less than 3 days at this temperature. The data obtained at 200 °C correspond to a heating time of 182 hours with all samples having equilibrated in less than 38 hours.

The nmr spectra were recorded on a Varian A-60 spectrometer after the samples had been quenched to room temperature, thus freezing the equilibrium corresponding to the heating temperature. Peak areas were determined by electronic integration or, in cases of closely overlapping peaks, by cutting out and weighing of Xerox copies of the spectra. The stoichiometric and statistical calculations were performed using computer programs developed by Dr. L. C. D. Groenweghe of this laboratory.

Results and Discussion

Exchange of bridging sulfur atoms and bromine atoms in mixtures of dibromodimethylsilane and hexamethylcyclotrisilthian proceeds readily between 150° and 200 °C with essentially no side reactions. The dimethylsilicon moiety under these conditions remains intact and the only observed processes are the breaking and making of silicon–bromine and silicon–sulfur bonds. In contrast to the analog chlorine system [2], no catalyst is required in the present equilibration reactions.

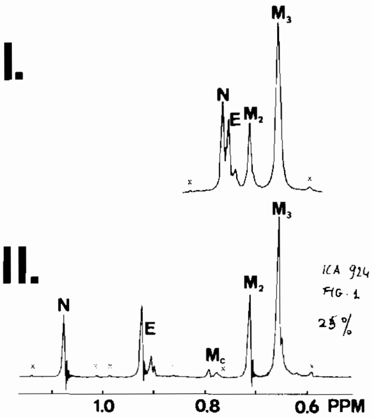
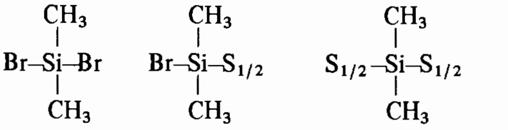


Figure 1. Proton nmr spectra of mixtures of $(CH_3)_2SiX_2$ and $[(CH_3)_2SiS]_3$ equilibrated at 200 °C. I: X = Cl; $R \equiv$ Cl/Si = 0.504; II: X = Br; $R \equiv$ Br/Si = 0.413. N = *neso* molecule, E = end groups, M_c = middle groups in chains, M_2 and M_3 = middle groups in the cyclic dimer and trimer, respectively. ^{29}Si satellites are denoted by X.

In agreement with the concepts developed earlier [1–3] exchange of bridging sulfur and bromine on dimethylsilicon moieties results in the generation of the following three types of structural building units:



$$\mathrm{Br{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}{-}Br} \qquad \mathrm{Br{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}{-}S_{1/2}} \qquad \mathrm{S_{1/2}{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}{-}S_{1/2}}$$

neso, n end group, *e* middle group, *m*

End and middle groups may associate to form linear and cycle molecules of theoretically almost infinite variety. At the temperature where the breaking and making of Si–Br and Si–S bonds occur readily, the variety of molecules present are in equilibrium with each other and the equilibria are determined by a set of equilibrium constants.

The equilibria within the chain molecules are determined by the equilibrium constant shown below.

$$K_1 = [n]\,[m \text{ in chains}]\,/\,[e]^2 \tag{1}$$

Theory [7, 8] has shown that the equilibria between chains and rings may be described quantitatively in terms of constants of the form shown below, with one constant for each ring size r (r = number of middle groups in ring molecule), where

$$K_r^o = \frac{[m_r]}{(1+D)[V_2 + (R/2)(V_o - V_2)]} \left[\frac{[e] + 2[m_c]}{2[m_c]}\right]^{\gamma} \tag{2}$$

m_r = middle groups in rings, m_c = middle groups in chains, D = dilution expressed in volumes of diluent per volume of neat sample. V_o and V_2 are the molar volumes in l/mol of the *neso* molecule (smallest molecule [7, 8]) and a middle group, respectively, R is the overall atom ratio [Br]/[Si] in the mixture and all bracketed building units are concentrations expressed in terms of mole fraction of the total building units.

Ring molecules of the ring sizes r and r′ (r′ > r) are related by ring–ring constants defined below.

$$K_{r',r}^{oo} = (K_{r'}^{o})^{r}/(K_{r}^{o})^{r'} = [m_{r'}]^{r}/[m_r]^{r'} \tag{3}$$

The ring–ring equilibria between hexamethylcyclotrisilthian (r′ = 3) and tetramethylcyclodisilthian (r = 2) have been studied earlier [9].

Nmr Spectra

A typical proton nmr spectrum of an equilibrated sample in the system $(CH_3)_2SiBr_2$–$[(CH_3)_2SiS]_3$ is shown in Fig. 1. For comparison purposes Fig. 1 also shows the nmr spectrum of a similarly equilibrated sample in the analog chlorine system, $(CH_3)_2SiCl_2$–$[(CH_3)_2SiS]_3$, clearly demonstrating the better resolution of the fine structure in the corresponding bromine system.

Nmr spectra like the one in Fig. 1 obtained for seven compositions which were equilibrated at 150 and 200 °C, respectively, were quantitatively evaluated in terms of nmr peak areas. These correspond to mol% building units and were compiled in Tables I and II. The assignment of the resonances to the listed building units and molecular fragments in Tables I and II was based on the rationale explained in previous papers [1–3]. Following the notation used in these earlier papers, combinations of the letters *e* and *m* are employed to describe groupings of the building units observed by nmr, with the bold-face letter denoting which building units correspond to the particular nmr resonance under consideration.

Equilibrium Constants

From the experimental nmr data the equilibrium constants of the form of eqs (1), (2) and (3) were calculated [7]. These values are presented in Table III together with the corresponding values for ΔH. The equilibrium constants in Table III have been used to calculate [7] theoretical equilibrium concentrations for the building units in the various environments seen in the nmr spectra. These data are listed in parentheses in Tables I and II below the corresponding experimental values. Inspection of these values shows that good agreement is generally achieved with these constants over the whole range of compositions and, in particular, the fit between experimental and theoretical equilibrium concentrations of middle groups in rings is most gratifying.

TABLE I. Equilibrium Data in Mol % Building Units in α, ω-Dibromopoly(dimethylsilthians) at 150 °C.

Assignment	*Neso*	End Groups			Middle Groups				
Chem. Shift[a] [ppm]	1.073	*ee*	*eme*	*emm*	*emc*	*emm*	$(m)_2$	$(m)_3$	*mmm*
$R \equiv [Br]/[Si]$		0.427	0.910	0.902	0.797	0.780	0.718	0.662	0.628
1.729[b]	78.0[c]	18.4	1.2	–	0.5	–	0.3	1.3	0.3
(1.756)[d]	(77.2)[e]	(20.1)	(1.2)	(0.1)	(0.6)	(0.1)	(0.4)	(0.4)	(0.0)
1.445	58.8	30.5	2.0	0.7	1.4	0.4	1.6	3.7	1.0
(1.508)	(57.9)	(30.7)	(3.7)	(0.5)	(1.9)	(0.5)	(1.7)	(3.2)	(0.0)
1.188	39.5	34.5	4.3	1.1	2.7	0.8	3.6	12.7	0.9
(1.189)	(39.2)	(32.8)	(6.2)	(1.5)	(3.1)	(1.5)	(3.9)	(11.9)	(0.2)
0.960	29.5	31.6	5.0	1.1	3.3	0.9	5.6	21.9	1.1
(0.967)	(29.0)	(29.7)	(6.9)	(2.1)	(3.5)	(2.1)	(5.6)	(21.1)	(0.3)
0.707	20.8	24.6	5.2	1.3	3.1	1.2	7.3	35.4	1.0
(0.727)	(19.8)	(24.1)	(6.6)	(2.5)	(3.3)	(2.5)	(7.6)	(33.7)	(0.5)
0.431	10.2	15.8	5.3	1.2	2.7	1.6	10.4	51.9	0.9
(0.427)	(10.3)	(14.9)	(4.9)	(2.4)	(2.4)	(2.4)	(10.1)	(52.7)	(0.6)
0.238	5.2	9.5	1.7	0.9	2.0	1.2	13.0	65.6	0.9
(0.225)	(5.0)	(8.0)	(2.9)	(1.6)	(1.4)	(1.6)	(11.8)	(67.6)	(0.5)

[a] Chemical shift in δ values with TMS = 0 as internal standard with downfield shifts being positive. The shifts were measured after equilibration in the composition $R = 0.960$. [b] Determined from the weights of the ingredients of the mixture. [c] From the nmr data. [d] Calculated from the nmr data of this table. [e] Calculated from the equilibrium constants $K_1^{(150°)}$, $K_2^{o(150°)}$ and $K_3^{o(150°)}$ using the R values from the ingredients.

TABLE II. Equilibrium Data in Mol % Building Units in α, ω-Dibromopoly(dimethylsilthians) at 200°C.

Assignment[a]	*Neso*	End Groups			Middle Groups				
$R \equiv [Br]/[Si]$		*ee*	*eme*	*emm*	*eme*	*emm*	$(m)_2$	$(m)_3$	*mmm*
1.726[b]	76.3[c]	17.7	1.0	–	0.8	–	1.5	1.0	1.8
(1.713)[d]	(74.0)[e]	(21.9)	(1.3)	(0.1)	(0.7)	(0.1)	(1.3)	(0.8)	(0.0)
1.445	59.0	28.7	2.0	0.4	1.2	0.4	3.6	4.0	0.8
(1.491)	(58.1)	(29.4)	(3.0)	(0.3)	(1.5)	(0.3)	(3.6)	(3.7)	(0.0)
1.233	44.2	31.0	2.5	1.8	2.4	1.0	7.0	9.3	1.0
(1.237)	(43.6)	(31.2)	(4.5)	(0.7)	(2.2)	(0.07)	(6.9)	(10.2)	(0.1)
0.960	30.6	29.5	4.1	1.1	2.9	1.1	10.1	19.8	0.9
(0.959)	(30.7)	(28.1)	(5.2)	(1.2)	(2.6)	(1.2)	(10.8)	(20.3)	(0.1)
0.707	21.1	22.7	3.6	1.7	3.1	1.0	13.8	32.2	0.7
(0.702)	(20.8)	(22.5)	(4.9)	(1.4)	(2.4)	(1.4)	(14.5)	(32.3)	(0.2)
0.431	10.6	16.1	2.4	1.6	2.8	1.2	18.7	45.8	0.8
(0.413)	(11.2)	(14.2)	(3.6)	(1.2)	(1.8)	(1.2)	(18.6)	(48.3)	(0.2)
0.238	5.5	8.7	1.7	1.2	1.7	0.6	23.6	56.5	0.6
(0.226)	(5.8)	(7.9)	(2.2)	(0.8)	(1.1)	(0.8)	(21.3)	(60.1)	(0.2)

[a] See Table I for the assignment of nmr peaks to building units. [b] Determined from the weights of the ingredients of the mixture. [c] From the nmr data. [d] Calculated from the nmr data of this table. [e] Calculated from the equilibrium constants $K_1^{(200°)}$, $K_2^{o(200°)}$ and $K_3^{o(200°)}$ using the R values from the ingredients.

The constants of Table III show that the distribution into building units in chains as defined by the equilibrium constant K_1 of eq. (1) for both temperatures is smaller than the random value, $K_{rand} = 0.25$. This indicates that the concentrations of end groups at equilibrium in this system is larger and those of $(CH_3)_2SiBr_2$ and the middle groups in chains is correspondingly smaller than expected for random sorting. The value of the constant K_1 of this system is similar to that in the corresponding chlorine system [1] studied earlier, where $K_1 = 0.13$ (200 °C). Exchange of Si–Br with Si–S bonds in mixtures of

TABLE III. Equilibrium Constants in α, ω-Dibromopoly(dimethylsilthians) at 150° and 200 °C.

	At 150 °C	At 200 °C	ΔH (kcal/mol)
K_1	0.11 ± 0.02	0.10 ± 0.02	–0.77
K_2^o	9.7 ± 3.1[a]	30 ± 3.5[a]	9.1
K_3^o	153 ± 7.3[a]	307 ± 19[a]	5.6
K_3^{oo}	21.4 ± 3.4[b]	3.5 ± 0.5[b]	–14.6

[a] In mol/liter. [b] In liter/mol.

$(CH_3)_2SiBr_2$–$(CH_3)_2Si(SCH_3)_2$, where the SCH_3 groups remain intact and $(CH_3)_2SiBr(SCH_3)$ is formed as the only product of the redistribution equilibration, is also non-random with the equilibrium constant $K = [(CH_3)_2SiBr_2]\,[(CH_3)_2Si(CH_3)_2]/[(CH_3)_2SiBr(SCH_3)]^2 = 0.049$ at 120 °C.

The ring-chain constants in Table III as well as the data in Tables I and II indicate that at equilibrium rings are greatly favored in this system. The constants for 200 °C in the present system agree with the ones determined in the analog chlorine system [1] at this temperature. Most of the middle groups present at equilibrium are parts of ring molecules, the dimer and trimer.

In agreement with the temperature dependence of the ring-chain equilibrium constants the total number of middle groups in ring molecules for a given composition increases with increasing temperature, *e.g.* for the composition R = 0.960 the percentage of middle group building units in rings at 150 °C is 27.5 and at 200 °C it is 29.9. Furthermore, in agreement with previous data [9] the equilibrium between the dimer and trimer ring molecules with increasing temperature shifts towards the dimer, *e.g.* for the composition R = 0.960 the ratio of middle groups in the dimer *versus* the trimer at 150 °C is 0.255, it is 0.512 at 200 °C.

Since most of the middle groups at equilibrium in this system are parts of ring molecules, the total number of middle groups in chains is very small as shown by the data of Tables I and II. The consequence of this, coupled with the fact that the equilibrium within the chain part of the system favors the formation of end groups, is that short chain molecules, such as *ee* and *eme*, predominate and there are not enough chain middle groups around to engage in the formation of longer chain molecules.

Thus, similar to the corresponding chlorine system, the equilibria in this system are dominated by the dimer and trimer ring molecules and short chain molecules. Long chain molecules, based on these data, are thermodynamically unstable and will equilibrate to form ring molecules and short chains.

Acknowledgement

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