Molecular architecture and conformation of macromolecules of novel polysilanes

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Molecular-weight parameters of new silane homo- and copolymers were analyzed. For all polymers, the M_w values are close ($(6.0-8.6) \cdot 10^4$), the curves of molecular weight distribution are unimodal, and $M_w/M_n = 2-2.5$. Cyclic fragments or those containing the —C≡C— groups make the major contribution to the polysilane chain rigidity.

Key words: synthesis, homopolymers, copolymers, molecular weight distribution, conformational parameters.

Polysilanes (PSL) are of great interest for both science and technology since they are highly sensitive to light and can be used as resists in photomicrography.[1—3] In addition, they are widely used as precursors of the SiC ceramics.[4,5] A number of works[6,7] are dedicated to the investigation of the effect of the molecular-weight parameters of PSL on their physicochemical properties; however, the role of conformation, shape, and size of the macromolecules has been little studied.[8,9] At the same time, the rigidity of the macromolecule chain, which depends on the chemical structure of the polymer unit and especially on that of the copolymer unit (molecular architecture), must to a great extent determine many physical properties of the polymeric material and, in particular, affect optical characteristics important for lithographic processes.

In this work, we performed conformational calculations and synthesized several PSL containing the $—Me_2Si—C_6H_4—SiMe_2—$ fragment common to all structural units and various fragments of different chemical structure (Table 1). Conformational parameters were calculated using the Monte Carlo method. The calculations for homopolymers were carried out assuming free rotation about virtual bonds following the known procedure,[10] and those for copolymers were carried out by the same method assuming that the probability of the addition of a particular unit is proportional to its mole fraction in the copolymer.[11]

Experimental

Homopolymers **1** and **7** (see Table 1) were synthesized by polycondensation[12] and polyaddition[13] reactions for the first time. The copolymers listed in Table 2 were synthesized from dichlorosilanes following the known procedure.[12] The molecular-weight characteristics of homo- and copolymers were determined by GPC on a Bruker LC-21 instrument. The curves of the change in weight fraction with increase in the molecular weight were recorded in toluene. The viscosities of homo- and copolymers synthesized were measured on an Ubbelohde viscosimeter in toluene at 25 °C, and that of homopolymer **7** was measured at different temperatures (at 20, 25, 30, and 50 °C).

Table 1. Conformational parameters of homopolymers at free rotation

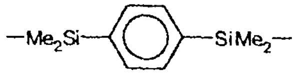
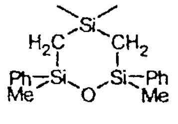
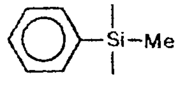
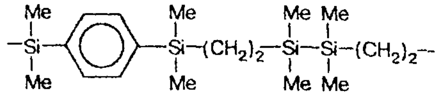
Homopolymer	Structural unit	l_0	A_{free}
		Å	
1		7.67	11.8
2	$—Me_2Si—CH_2—SiMe_2—$	5.05	5.3
3	$—Me_2Si—CH_2—CH_2—SiMe_2—$	6.35	5.1
4	$—Me_2Si—C≡C—SiMe_2—$	6.15	9.6
5		2.01	7.7
6		1.93	5.9
7		11.6	6.9

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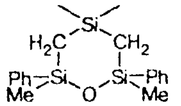
Table 2. Conformational parameters of copolymers at free rotation

Copolymer	Copolymer unit	Chain fragment	l_0	A_{free}
			Å	
I	1—2	$-CH_2-$	6.81	9.9
II	1—3	$-(CH_2)_2-$	7.23	9.7
III	1—4	$-C≡C-$	7.17	10.9
IV	1—5		5.78	11.4

Results and Discussion

The structural units, contour lengths of the units (l_0), and values of the Kuhn segments calculated assuming free rotation (A_{free}) for homopolymers are given in Table 1. From Table 1 it follows that the conformational flexibility of polymer 7 is higher than that of polymer 1. A gradual change in the structural unit of polymer 1 due to introduction of fragments containing an sp^3-hybridized C atom, such as $-CH_2-$ or $-(CH_2)_2-$ groups, results in an increase in the chain flexibility: the Kuhn segment A_{free} becomes halved. At the same time, rigid fragments, such as $-C≡C-$ and the cyclic fragment sharing one of its Si atoms with the chain, decrease its rigidity to a lesser extent.

Conformational parameters for statistical copolymers composed of two types of units, a unit of homopolymer 1 and a unit of one of the other homopolymers, are given in Table 2. The ratio of the components in all copolymers was the same (2 : 1). The data in Table 2 confirm the dependence of the chain rigidity on the unit architecture found for homopolymers: the introduction of flexible fragments (copolymers **I** and **II**) causes a decrease in the chain rigidity, whereas the introduction of rigid fragments (copolymers **III** and **IV**) causes an increase in the chain rigidity; moreover, it appears to be sensitive to the fraction of these fragments in the chain.

Table 3. Experimental values of molecular and conformational parameters of copolymers

Copolymer	M_w	M_w/M_n	M.p. /°C	[η] /dL g^{-1}	A_{exp} /Å	σ^2
I	6150	2.4	73	0.062	11.8	1.2
II	8600	2.3	60	—	—	—
III	8570	2.5	67	0.078	11.6	1.1
IV	6200	2.0	86	0.600	16.2	1.4

The calculations were performed assuming free rotation. It was of interest to test the validity of the regularities established for actual polymers. To this end, we synthesized the homopolymers whose structural units are given in Table 1.

For all copolymers, the M_w values are small and close to each other (Table 3). The curves of the molecular weight distribution (MWD) are unimodal (Fig. 1, curve *1*) and the M_w/M_n ratios are approximately equal to 2 (see Table 3), which corresponds to the most probable distribution. This suggests a possible polycondensation mechanism of the formation of macromolecules of the copolymers.

Analysis of the molecular parameters of homopolymer 1 (M_w = 6580, M_w/M_n = 2.5, [η] = 0.08 dL g^{-1}, and unimodal MWD curves) showed that their values are close to those of copolymers. A small peak in the high-molecular region is observed (see Fig. 1, curve *6*)

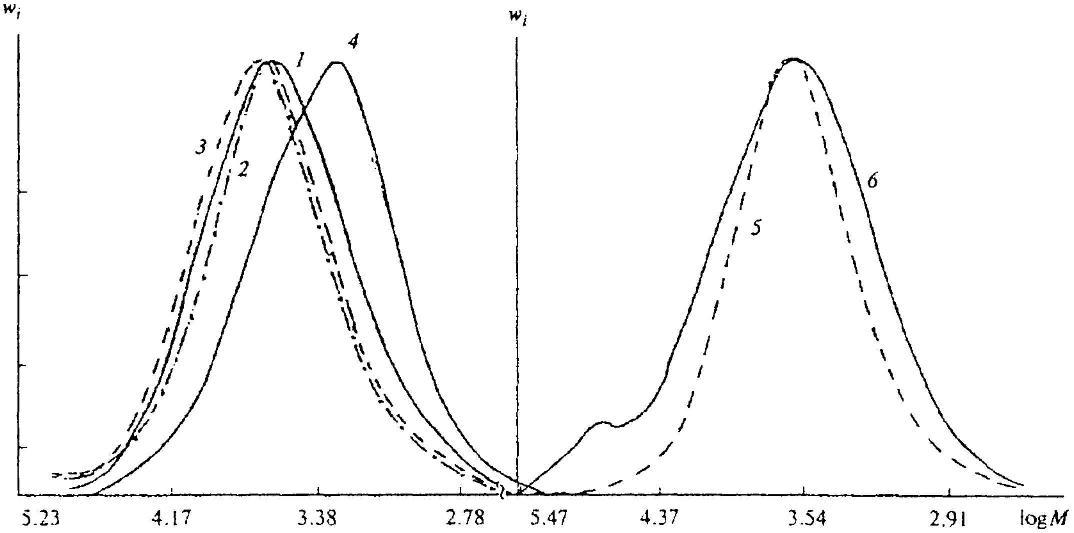


Fig. 1. Curves of the molecular weight distribution for homopolymers 1 and 7 (curves *1* and *6*, respectively) and copolymers **I—IV** (curves *2—5*, respectively).

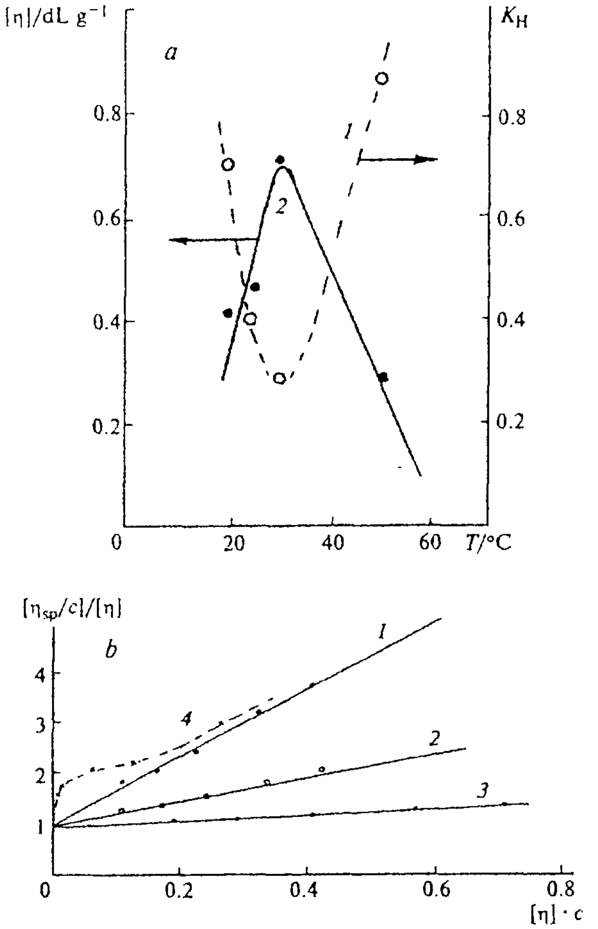


Fig. 2. *a*. Dependences of the Huggins constant (K_H) (*1*) and viscosity ([η]) (*2*) of homopolymer 7 on the temperature of toluene solution. *b*. Dependence of viscosity ([η]) on the concentration of the solution of homopolymer 7 in toluene at 20 (*1*), 25 (*2*), 30 (*3*), and 50 (*4*) °C.

for homopolymer 7 (see Table 1), which might be associated with the higher molecular weight M_w = 12000, an M_w/M_n ratio of 4, and [η] = 0.425 dL g^{-1}.

The obtained experimental data on the molecular weights and viscosities for homo- and copolymers made it possible to compare the behavior of macromolecules in solution and to estimate the values of conformational (A_{exp} and $\sigma^2 = A_{exp}/A_{free}$) and thermodynamic (the Huggins constant K_H) parameters of the polymeric systems studied.

It is noteworthy that the curves of the dependences of [η] and K_H on temperature for solution of homopolymer 7 in toluene have extrema, which indicates conformational transitions (see Fig. 2, *a*). This is characteristic of the *trans*-conformation of the chain (a helical conformation confirmed for PSL chains by several authors and in our previous work[8] taking a silane copolymer as an example). For the PSL studied, the dependence of change in the reduced viscosity on the concentration at high temperature (50 °C) appeared to be nonlinear (see Fig. 2, *b*). This can be explained by unwinding of the helix at high dilution.

Table 4. Calculated values of helix width (*b*) of macromolecules of polymers

Polymer	M_0	n^2	*b* /Å
		Copolymers	
I	760	64	2.35
II	774	121	—
III	770	64	2.3
IV	818	100	2.3
		Homopolymers	
1	315	490	1.2
2	364	1090	1.6

Taking into account this fact and considering, by convention, homo- and copolymers as semirigid chains, it is possible to calculate the helix width (*b*) using the procedure described previously:[13]

$$b = \left(\frac{[\eta]\,16M_0\ln n}{\pi N_A n^2}\right)^{1/3},$$

where *n* is the number of monomeric units and N_A is the Avogadro constant. As can be seen from the data in Table 4, the helix widths of all copolymers are almost equal (~2.3 Å) and are larger than those of homopolymers.

Taking into account that the values of the molecular weights, viscosities, and helix widths of the copolymers studied are close to each other and that their MWD are unimodal, and the M_w/M_n ratios are small and approximately equal, it was reasonable to make a comparative estimation of conformational parameters of the copolymers based on the values of the characteristic viscosity [η] in toluene at 25 °C and M_w.

According to the Stockmayer—Fixman equation,[14]

$$[\eta]/M^{1/2} = \Phi_0(h_0{}^2/M)^{3/2} + 0.51BM^{1/2},$$

where Φ_0 is the Flory coefficient, $h_0{}^2$ is the size of the macromolecule, *B* is the long-range action parameter, the quantity $[\eta]/M^{1/2}$ is proportional to K_H, and

$$h_0{}^2/M = \left(\frac{[\eta]/M^{1/2}}{\Phi_0}\right)^{2/3}.$$

In turn, we have for the Kuhn segment $A_{exp} = (h_0{}^2/M)M_L$, where $M_L = M_0/l_0$. From the data in Table 3 it can be seen that the A_{exp} values for the three copolymers studied are nearly equal and that the hindered rotation parameter (σ) is small ($\sigma^2 \approx 1$), which is characteristic of PSL with the *trans*-conformation of the chain.

Thus, our investigation of the effect of architecture on the conformation of the macromolecule carried out assuming its free rotation (with no substituents, A_{free}) and under actual conditions (in toluene solution, A_{exp}) showed that the rigidity of macromolecules increases upon introduction of cyclic fragments both into the main chain and as side substituents and decreases appreciably if the $-CH_2-$ and $-(CH_2)_2-$ groups are present in the main chain. It was established that the chain rigidity of silane copolymers can be either increased or decreased by successively changing the structure of the unit by introducing fragments of different rigidity into the main chain. The Kuhn segment calculated assuming free rotation can be used as a criterion for evaluation of the chain rigidity.

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