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Mechanochemical Synthesis of Poly(germanium and tin organosiloxanes)

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Abstract—The mechanochemical reaction of polyphenylsiloxane with tin and germanium oxides gives rise to soluble tin and germanium phenylsiloxanes. Effect of the nature of the oxide and of the starting reagent ratio on the yield and composition of metal phenylsiloxanes was studied. The reaction products were studied by IR spectroscopy and X-ray phase analysis.

Earlier we effected mechanochemical synthesis of poly(iron organosiloxanes) from sodium salts of phenylsilanetriol and metal chlorides [1], as well as poly(copper organosiloxanes) from copper acetylacetonate and organosilicon diols [2]. In both cases classical methods of synthesis of poly(metal organosiloxanes) were used: exchange decomposition and heterofunctional condensation. However, the use of these methods under mechanochemical activation conditions is limited by the appearance of a ballast component that is necessary to remove.

In the present work we studied the possibility of mechanochemical synthesis of poly(tin and germanium organosiloxanes) on the basis of tin(IV) and germanium(IV) oxides that have never been used for this purpose. The choice of tin(IV) and germanium(IV) oxides as starting materials was motivated by the fact that they make it possible to form an SiOM bond without appearance of a ballast component and to save on solvents in isolation.

The cleavage of the siloxane bond in polyphenylsiloxane with tin alkoxides in organic solvents has been reported in [3]. We suggested that under mechanical activation conditions tin oxide would prove a useful cleaving agent, since the effective negative charge on the oxygen atom in this compound is, like in tin alkoxides, rather high. Germanium oxide is more acidic than silicon oxide, and, therefore, we considered it worthwhile to try it as a Si–O cleaving agent.

All syntheses were based on Si–O bond cleavage with oxides.

$$m(C_6H_5SiO_{1.5})_n + nMO_2 \longrightarrow [(C_6H_5SiO_{1.5})_mMO_2]_n,$$

M = Ge, Sn; m = 1, 4; for n, see Table 1.

As seen from the elemental analyses of the synthesis products (Tables 1 and 2), we failed to reach the preset Si/M ratio.

Comparing exp. nos. 1^i and 3^i, where different metals and the same starting Si/M ratios (4 : 1) were used, we can see that the percentage of soluble fraction in these reactions is almost independent of the nature of the metal and probably depends on the starting cyclolinear structure of the polyphenylsiloxane, that is preserved in the soluble fraction even after metalation.

However, the rate in which a metal enters into the siloxane chain is obviously dependent on the nature of the metal. The mole fraction of germanium with respect to silicon after 0.5 (exp. no. 3^1) and 1 h (exp. no. 3^2) is ~2.5 times larger that the respective value for tin (exp. nos. 1^1 and 1^2). After 2-h activation (exp. nos. 1^3 and 3^3) the Si/M ratio in poly(tin phenylsiloxane) and poly(germanium organosiloxane) reaches ~9, which suggests incorporation of one metal atom per three trisiloxane units. The metal content of the polymeric chain only slightly increases as the reaction time is prolonged to 3 h. But here, too, with tin, the metal fraction is larger than with germanium (cf. exp. nos. 1^4 and 3^4).

The gel chromtograms of the soluble fractions in exp. nos. 1^i and 3^i are given in Figs. 1 and 2. At the same activation time, poly(tin organosiloxanes) are more polydisperse than poly(germanium organosiloxanes). This difference is best pronounced at the synthesis times 0.5 (exp. nos. 1^1 and 3^1) and 3 h (exp. nos. 1^4 and 3^4). Apparently, the slower incorporation of tin into the siloxane chain favors cleavage of the latter, especially in the initial and final stages of formation of the metal–siloxane bond, and induces addition of the terminal stannoxane fragment.

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Table 1. Elemental composition of germanium-containing products

Exp. no.	Si/Ge ratio	Time, h	Fraction	Relative fraction, %	Found, %				Calculated for $[(PhSiO_{1.5})_mGeO_2]_n$, %			
					C	Ge	Si	Si/Ge	C	Ge	Si	*n*
3^1	4 : 1	0.5	Soluble	78	54.6	5.2	24.5	12.5 : 1.0	52.4	4.2	20.4	~1.0
			Insoluble	23	0.8							
3^2	4 : 1	1	Soluble	81	52.8	5.3	22.4	11.4 : 1.0	51.9	4.6	20.2	~1.0
			Insoluble	19	0.7							
3^3	4 : 1	2	Soluble	83	55.7	5.6	20.9	9.6 : 1.0	51.4	5.4	20.0	>3.0
			Insoluble	17	0.6							
3^4	4 : 1	3	Soluble	86	51.1	7.5	20.0	7.0 : 1.0	50.0	7.2	19.5	>3.0
			Insoluble	15	0.8							
4^1	1 : 1	0.5	Soluble	60	45.0	14.5	16.8	3.0 : 1.0	43.9	14.8	17.1	~3
			Insoluble	40	2.0	65.0	4.6	1.0 : 5.5	10.2	56.6	3.9	
4^2	1 : 1	1	Soluble	64	44.7	14.8	16.2	2.9 : 1.0	43.6	15.2	16.9	~3
			Insoluble	36	2.4	64.0	5.0	1.0 : 4.9	11.2	55.4	4.3	
4^3	1 : 1	2	Soluble	68	44.5	15.2	16.0	2.8 : 1.0	43.3	15.3	16.8	~4
			Insoluble	32	2.3	63.5	5.5	1.0 : 4.5	12.0	54.4	4.6	
4^4	1 : 1	3	Soluble	70	43.4	15.7	15.8	2.5 : 1.0	41.9	16.9	16.3	>4
			Insoluble	30	2.4	62.8	6.0	1.0 : 4.3	12.4	53.9	4.8	
4^5	1 : 1	4	Soluble	70	43.5	16.0	15.5	2.4 : 1.0	41.4	17.7	16.1	>4
			Insoluble	30	0.5	62.0	6.2	1.0 : 3.9	13.4	52.7	5.2	–

Table 2. Elemental composition of tin-containing products

Exp. no.	Si/Ge ratio	Time, h	Fraction	Relative fraction, %	Found, %				Calculated for $[(PhSiO_{1.5})_mSnO_2]$, %		
					C	Si	Sn	Si/Sn	C	Si	Sn
1^1	4 : 1	0.5	Soluble	78	54.0	21.0	2.8	31.6 : 1	53.8	20.9	2.8
			Insoluble	22	5.7	2.2	70.7	1 : 7.5	5.7	2.2	70.7
1^2	4 : 1	1	Soluble	80	53.6	20.8	3.2	27.5 : 1	53.4	20.8	3.2
			Insoluble	20	2.8	1.1	74.8	1 : 16.2	2.8	1.1	74.8
1^3	4 : 1	2	Soluble	87	49.5	19.2	8.9	9.2 : 1	49.5	19.2	8.9
			Insoluble	14	3.1	1.2	74.6	1 : 14.6	3.1	1.2	74.6
1^4	4 : 1	3	Soluble	88	49.5	19.0	9.6	8.4 : 1	49.1	19.1	9.6
			Insoluble	12	3.0	1.0	75.8	1 : 17.9	3.0	1.0	75.8
2^1	1 : 1	0.5	Soluble	47	52.0	20.3	5.4	15.9 : 1	51.9	20.2	5.3
			Insoluble	53	2.7	1.0	74.9	1 : 16.8	2.7	1.1	74.9
2^2	1 : 1	1	Soluble	48	51.0	19.9	6.9	12.25 : 1	50.9	19.8	6.9
			Insoluble	52	2.6	1.0	75.0	1 : 17.5	2.6	1.0	75.0
2^3	1 : 1	2	Soluble	49	49.8	19.3	9.0	9.1 : 1	49.5	19.3	9.0
			Insoluble	51	2.5	1.0	74.7	1 : 17.6	2.6	1.0	75.1

The four-fold increase of the molar fraction of metal oxide in the starting compounds (Si/M = 1) in exp. nos. 2^i–4^i provides evidence for the suggestion that in the case of tin oxide the siloxane chain cleaves faster than incorporates tin. Further evidence for this suggestion comes from the fact the soluble fraction is much diminished, while its maximum tin content after 2-h activation is almost that same as the starting Si/Sn

ratio of 4 (exp. nos. 1^3 and 2^3). Moreover, the reaction products are more polydisperse, as follows from gel chromatography (Fig. 3).

The soluble poly(tin phenylsiloxanes) are formed as glassy light yellow materials in all experiments. The IR spectra of these compounds contain bands at 1080 and 1020 cm^{-1}, belonging to vibrations of the Si–O–Si bonds in cyclolinear structures. The Si–C_6H_5 bond was identified by the bands at 1431 and 1137 cm^{-1}. Vibrations of the Si–O bond in the Si–O–Sn fragment appear at 980 cm^{-1}.

The insoluble fractions in exp. nos. 2^1–2^3, like in exp. nos. 1^1–1^4, according to the elemental and X-ray phase analyses and IR spectra, comprise unreacted tin oxide with a small admixture of structured organosilicon derivatives. The IR spectra almost lack bands due to Si–O– Si vibrations. There is only a broad Sn–O–Sn vibration band at 614–639 cm^{-1}. A different pattern is observed with germanium oxide. The soluble fraction is decreased to a lesser extent compared with exp. no. 3^i, and the polymeric chain incorporates much more germanium. After 3 h, the Si/Ge ratio attains 2.5. As the activation time is increased to 4 h, the germanium content of the polymeric chain does no increase, but the peak on the gel chromatogram (Fig. 4) shifts to lower molecular weights and gets broader, implying prevalence by this time of cleavage of the metal siloxane chain over its formation.

The soluble germanium phenylsiloxanes are light brown glassy materials. The IR spectra of all soluble fractions are almost identical. There are bands at 1020–1080 cm^{-1}, characteristic of the Si–O–Si bond. The Si–C6H5 bond appears at 1430 and 1134 cm^{-1} and the Ge–O bond in the Ge–O–Si fragment, at 998 cm^{-1}.

The insoluble fractions in all experiments (light gray powders) comprise, like with tin, unreacted germanium oxide and products of partial decomposition of polyphenylsiloxane. This is confirmed by the elemental analyses and IR spectra that almost lack polysiloxane Si–O–Si and Si–C_6H_5 and aromatic C–H absorption bands. The observation of a strong ≻Ge–O–Ge≺. band at 880 cm^{-1}, too, provides evidence for this suggestion.

EXPERIMENTAL

The IR spectra were registered on a Perkin–Elmer Spectrum-BX instrument in the range 400–4000 cm^{-1}. Analysis for carbon and hydrogen was performed on a Flash EA-1112 CHN/MAS-200 analyzer. X-ray analysis of insoluble fractions was performed on a DRON-2 diffractometer (CuK_α radiation).

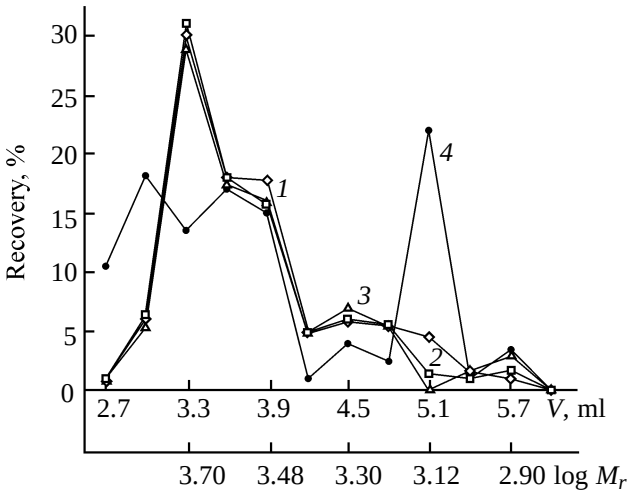

Fig. 1. Gel chromatograms of soluble fractions of tin phenylsiloxanes (Si/Sn = 4). Here in hereinafter, curve numbers correspond to experiment numbers.

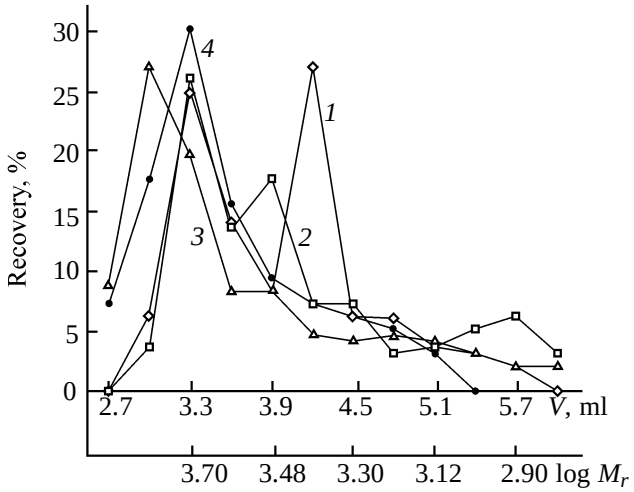

Fig. 2. Gel chromatograms of soluble fractions of germanium phenylsiloxanes (Si/Ge = 4).

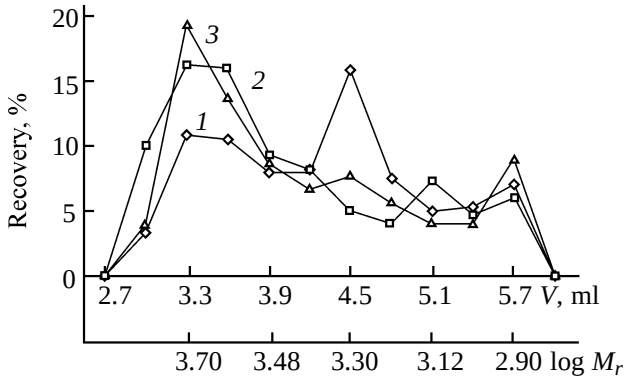

Fig. 3. Gel chromatograms of soluble fractions of tin phenylsiloxanes (Si/Sn = 1).

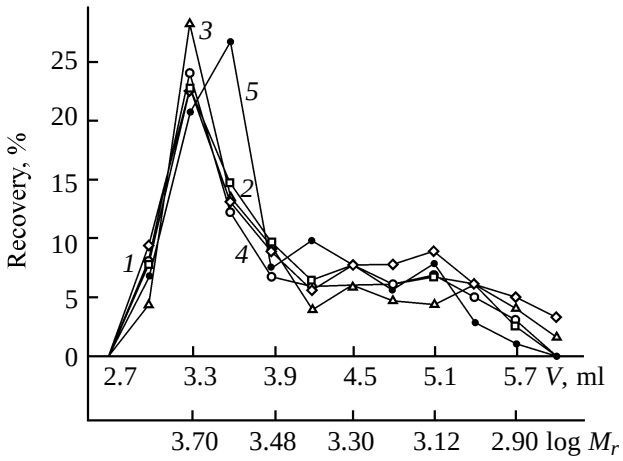

Fig. 4. Gel chromatograms of soluble fractions of germanium phenylsiloxanes (Si/Ge = 1).

Sixteen experiments with varied activation time, starting Si/M, and oxides were performed. Mechanochemical activation was performed in a vibration activator at 2.5 Hz. The load-to-packing weight ratio was ~2.0. The packing was steel balls 12 mm in diameter.

In exp. nos. 1^1, 1^2, 1^3, and 1^4 with varied activation time (0.5, 1, 2, and 3 h, respectively), 6.45 g of polyphenylsiloxane was mixed with 1.88 g of tin(IV) oxide. The starting Si/Sn ratio was 4 : 1. In exp. nos. 2^1 (0.5 h), 2^2 (1 h), and 2^3 (2 h), polyphenylsiloxane, 1.29 g, was mixed with 1.507 g of tin(IV) oxide. The starting Si/Sn ratio was 1 : 1.

With germanium(IV) oxide, the same Si/M ratios were used: 4 : 1 (exp. nos. 3^1–3^4) and 1 : 1 (exp. nos. 4^1–4^5).

The synthesis time was varied from 0.5 (exp. nos. 3^1 and 4^1) to 1 (exp. nos. 3^2 and 4^2), 2 (exp. nos. 3^3 and 4^3), 3 (exp. nos. 3^4 and 4^4), and 4 h (exp. no. 4^5). In exp. nos. 3^1–3^4, the reaction was performed with 5.16 g of polyphenylsiloxane and 1.046 g of germanium(IV) oxide and in exp. nos. 4^1–4^5, with 1.29 g of polyphenylsiloxane and 1.046 g of germanium(IV) oxide.

After mechanochemical activation, the reaction mixture was separated into soluble and insoluble fractions by extraction with toluene in a Soxhlet apparatus. The dispersity and polymerization degree of the soluble fractions were determined by gel chromatography (column 750 × 10 mm) on a colopymer of styrene with 2% of divinylbenzene (grain size 0.08–1 mm, column free volume 24 ml, upper molecular weight limit 5000).

The general formula of the synthesized products was $[(C_6H_5SiO_{1.5})_mMeO_2]_n$ (M = Ge^{+4}, Sn^{+4}; *m* varied over a wide range).

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