ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 6, pp. 1487–1490. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © N.P. Shapkin, A.A. Kapustina, S.V. Gardionov, I.G. Khal'chenko, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 6, pp. 1022–1026.

Interaction of Polyphenylsiloxane with Magnesium Acetylacetonate

N. P. Shapkin, A. A. Kapustina, S. V. Gardionov, and I. G. Khal'chenko

Far Eastern Federal University, ul. Sukhanova 8, Vladivostok, 690000 Russia
e-mail: npshapkin@gmail.com

Received January 12, 2015

Abstract—Interaction of polyphenylsiloxane with magnesium acetylacetonate in boiling toluene has been studied. The products isolated via extraction and fractional precipitation have been characterized with elemental analysis, IR spectroscopy, X-ray diffraction analysis, and thermal analysis. The reaction products are polymers containing acetylacetonate group at magnesium atom. Structure of the major product has been suggested.

Keywords: polyphenylsiloxane, magnesium acetylacetonate, Millet–Boyer method, bridging bonding, poly(phenylmagnesium)siloxane

DOI: 10.1134/S1070363215060225

Interaction of metal salts with monomeric and polymeric organylsiloxanes in organic medium has been fairly well studied [1]. In particular, the preparation of poly(organylmetal)siloxanes via splitting of the polymeric siloxanes has been described [2]. Furthermore, the cleavage of the siloxane bond can occur under the action of phosphorus oxide or phosphorus-containing acids [3] as well as of boric acid [4]. The interaction of iron acetylacetonate with polydimethylsiloxane in toluene is known to yield the product containing Si–O–Fe fragments [5]. The interaction of metal oxides with polyphenylsiloxane under conditions of mechanochemical activation has yielded (phenylmetal)siloxanes as well [6].

Both polyphenylsiloxane and magnesium acetylacetonate are fairly accessible substances; therefore, the method to prepare metalated siloxanes based on these precursors would be promising in view of the industrial application. In particular, the product of such reaction can be used as a tribochemical additive for engine oils [7].

This work aimed to study the interaction between magnesium acetylacetonate with polyphenylsiloxane. The reaction was carried out in boiling toluene at the equimolar ratio of the metal complex and the polymer hydroxyl groups. The expected reaction route was as follows (Hacac standing for acetylacetone).

$$nx(\mathrm{acac})_2\mathrm{Mg} + \{[\mathrm{PhSiO}_{1.5}]_{(1-x)}[\mathrm{PhSi(OH)O}]_x\}_n \rightarrow \{[(\mathrm{PhSiO}_{1.5})_{(1-x)}][\mathrm{PhSi(OMgacac)O}]_x\}_n + nx(\mathrm{Hacac}).$$

Four fractions of the reaction product were isolated via fractional precipitation. Fraction 1 (the major one) was insoluble even in hot toluene, fraction 2 precipitated from the toluene solution upon cooling, fraction 3 precipitated from the toluene solution after addition of an equal volume of heptane, and fraction 4 was soluble even in the toluene–heptane mixture and was isolated via evaporation of the solvent. Elemental analysis data for the isolated fractions are collected in the table.

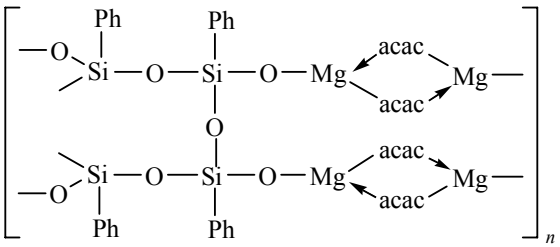
IR spectrum of the fraction 1 (Fig. 1, curve *1*) contained the following absorption bands (ν, cm^{-1}): 1598 (C=O→Mg), 1520 (C=C), 2924 and 2991 ($C–H_{acac}$), 1265 and 1402 [$\delta(C–H_{acac})$], 3077 ($C–H_{Ar}$), 1133 (Si–C), 1020–1060 (Si–O–Si), 497 [δ(Si–O)], and 430 [δ(Mg–O)].

According to the above-given reaction scheme, the acetylacetonate ligand could be replaced in the magnesium complex only with the Si–O–H group. At the same time, the starting polyphenylsiloxane contained less of hydroxy groups as compared to the amount of silicon atoms. Therefore, magnesium content in the product should have been lower than that of silicon, provided that the reaction occurred via the suggested scheme. The elemental analysis data (see table) confirmed that the fraction 1 contained equal amounts of Si and Mg. The excess of magnesium in the product could not be due to the admixture of the unreacted magnesium acetylacetonate: the latter is

Elemental analysis of the isolated fractions of the polymer

Fraction	Yield, %	Found, wt %			Si : Mg, mol/mol
		C	Si	Mg	
1	42.5	44.5	8.9	7.8	1.0
2	17.7	46.7	3.4	5.3	5.6
3	12.3	52.7	20.7	1.4	10.0
4	11.0	55.1	21.7	0.2	93.0

soluble in toluene, and the fraction 1 precipitated from hot toluene solution. Evidently, the only explanation of the elemental analysis data is the presence of the units containing several magnesium atoms bound via the bridging acetylacetonate ligands in the reaction product. The available data did not allow for unambiguous identification of structure of the product contained in the fraction 1. The possible structure of the condensed fragments is as follows:



It was reasonable to suggest that the fractions 2–4 were also the products of partial substitution of the silanol group hydrogen atoms with the Mg(acac) fragments; the substitution degree decreasing in the 2–4 series (cf. the Si : Mg ratio in the table). Indeed, IR spectra of the fractions 3 and 4 (Fig. 1, curves *3* and *4*) contained the weak bands corresponding to the Mg–O vibrations (440 cm^{-1}) and were similar to that of the initial polyphenylsiloxane (Fig. 1, curve *6*), whereas the spectrum of the fraction 2 (Fig. 1, curve *2*) revealed the gradual transition from the spectrum of the starting polymer to the spectrum of the magnesium-enriched fraction 1. Accounting for the products solubility, we suggested that the fractions 2–4 contained small amounts of the acetylacetonate fragments.

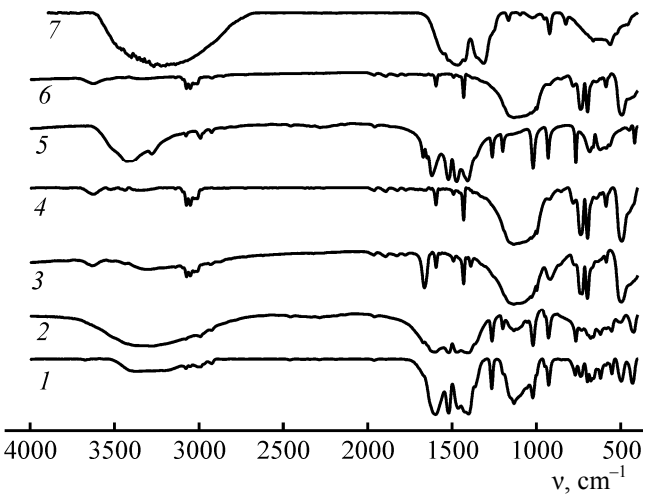


Fig. 1. IR spectra (*1–4*) of the fractions 1–4, (*5*) initial $Mg(acac)_2$, (*6*) starting polyphenylsiloxane, and (*7*) $Mg(acac)_2$ after annealing at 250°C.

Thermal analysis of the fraction 1 revealed the two exothermic effects assigned to oxidation of the acetylacetonate fragments (316°C) [8] and of the phenyl groups (516.6°C) [9]. The elimination of he bound water from the sample occurred in two stages, at 77 and 143°C. The high-temperature residue after the annealing was 32.8 wt % (TGA data), and the sum of SiO_2 and MgO mass fractions was 32.1 wt % (elemental analysis data).

X-ray diffraction analysis of the fraction 1 (Fig. 2, curve *1*) revealed the presence of reflections evidencing the crystalline structure of the specimen. The reflection at θ of 4.5° corresponded to the d_{100} interlayer spacing. The data allowed calculation of the product chain section area *S* using the Miller–Boyer method [11].

$$\log d = K_1 + K_2 \log S.$$

We have earlier demonstrated [12] that the K_1 = 0.06 and K_2 = 0.61 values can be used to calculate the cross-section area of polyphenylsiloxanes. The chain cross-section area of the product contained in the fraction 1 was of 2.69 nm^2, significantly larger than that of the parent polyphenylsiloxane (1.08 nm^2 [12]); the cross-section increase was seemingly due to the presence of bulky acetylacetonate groups. The suggested structure of the polymer in the fraction 1 presumed that each magnesium atom bound to the silanol group of

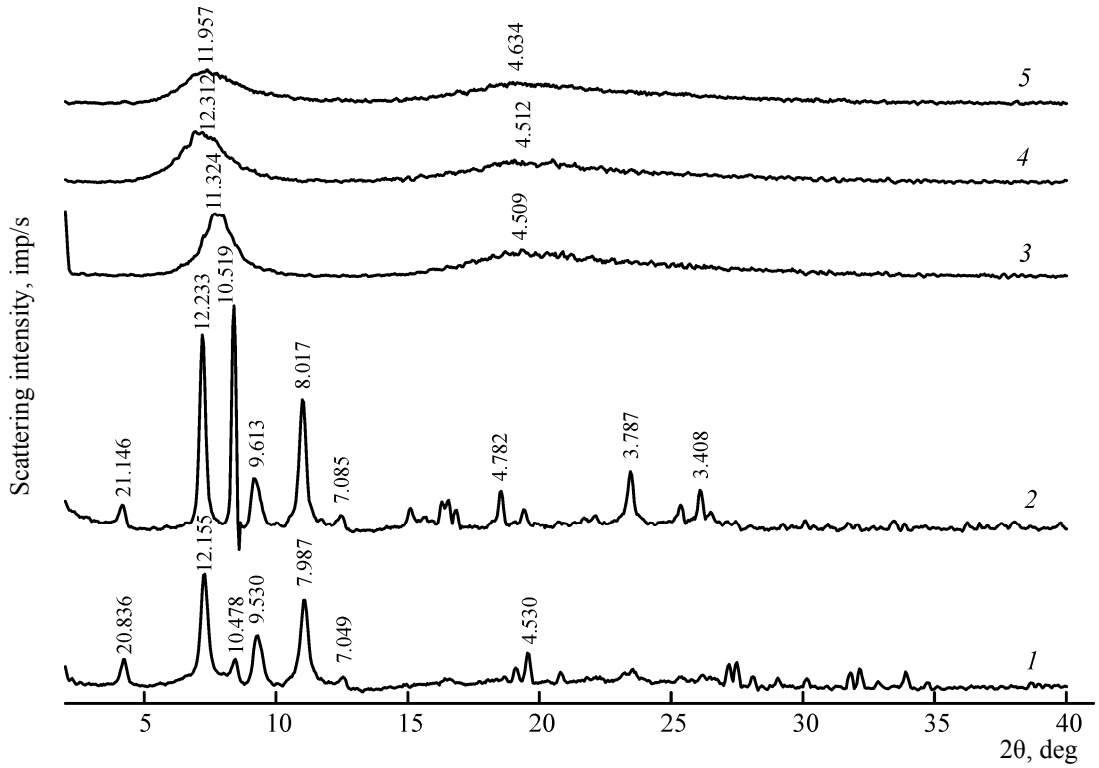


Fig. 2. X-ray diffraction patterns (*1–4*) of the fractions 1–4 and (*5*) starting poly(phenyl siloxane).

the polymer could be linked to other Mg atoms via the acetylacetonate bridges. That was indirectly confirmed by the polymerization of magnesium acetylacetonate observed at relatively low temperature (cf. IR spectra *5* and *7* in Fig. 1; after the thermal treatment all the observed bands were broadened, evidencing the formation of the bridging bonds [13]). Similar bridged structures have been found in the reaction mixture after prolonged boiling of rhenium β-diketonate [14].

Thermal analysis of the fraction 2 confirmed formation of the polymeric magnesium acetylacetonate: stepwise condensation of the acetylacetonate fragments, their oxidation, and finally the phenyl groups oxidation were observed over the temperature range of 391–535°C. The behavior of pure magnesium acetylacetonate was similar: the two exothermic effects were observed, corresponding to partial oxidation of the monomeric complex and oxidation of the polychelate at higher temperature. The presence of the magnesium *bis*-chelate in the fraction 2 was confirmed by the X-ray diffraction analysis data (Fig. 2, curve *2*).

The fractions 3 and 4 contained significantly less of magnesium and acetylacetonate groups (see table). The fractions X-ray diffraction patterns were similar to that of the polyphenylsiloxane [10]. Accounting for the fractions solubility, we suggested that they contained the products with negligibly low degree of the silanol groups modification.

To summarize, the interaction of polyphenylsiloxane with magnesium acetylacetonate yielded various poly(phenylmagnesium)siloxanes; the least soluble fraction contained magnesium atoms linked via the bridging acetylacetonate ligand, and the most soluble fractions contained the polymer with low degree of the silanol groups modification.

EXPERIMENTAL

All the chemicals were of "analytically pure" grade, supplied by Reakhim. DMF and acetylacetone were distilled under reduced pressure; other substances were used as received. IR spectra of KBr pellets were recorded using a Spectrum 1000 (PerkinElmer) spectrometer. X-ray diffraction analysis was performed using an Advance D8 (Bruker) diffractometer (CuK_α, $2° < 2\theta < 90°$). Magnesium content was determined via atomic emission spectroscopy using a parallel JCPE 9000 (Shimadzu) spectrometer with inductively coupled plasma (after carbon determination by the wet ashing method). Thermal analysis was performed using a DTG-60H (Shimadzu) derivatograph in air at the heating rate 10 deg/min (25–1000°C). Gel permea-

tion chromatography analysis was run as described in [17].

Magnesium acetylacetonate [15]. A solution of 20 g of acetylacetone (0.2 mol) in 50 mL of diethyl ether and then 13.6 mL of aqueous ammonia (25 wt %) were added to a solution of 26.4 g (0.1 mol) of $MgSO_4 \cdot 7H_2O$ in 70 mL of water. The mixture was heated at 80°C during 30 min; the formed white clotted precipitate was filtered off, dried to constant mass in air at room temperature, and recrystallized from the 1 : 1 chloroform–ethanol mixture. Yield 81%. Found, %: C 45.9; Mg 9.6. $(C_5H_7O_2)_2Mg \cdot 2H_2O$. Calculated, %: C 46.5; Mg 9.3.

Polyphenylsiloxane [16]. 800 mL of water and 400 mL of diethyl ether were put into a three-necked flask equipped with mechanical stirrer, reflux condenser, and dropping funnel; the flask was cooled with ice. 250 mL (1 mol) of phenyltrichlorosilane in 250 mL of diethyl ether was added at vigorous stirring, and the mixture was stirred during 2 h. The organic layer was separated, washed with water to the neutral reaction, and dried over calcium chloride. Then the solvent was removed, and the product was dried to constant mass. Yield 127 g (98.4%). Found, wt %: C 55.3; Si 21.2. $M > 5000$ (GPC). $\{[C_6H_5Si(OH)O]_x[C_6H_5SiO_{1.5}]_{(1-x)}\}_n$, $x = 0.125$ (the C content), 0.365 (the Si content).

Interaction of polyphenylsiloxane with magnesium acetylacetonate. A mixture of 16 g of magnesium acetylacetonate, 300 mL of toluene, and 15.9 g of polyphenylsiloxane was refluxed during 8 h. The precipitate formed after cooling to ambient temperature was filtered off (13.2 g). The crystalline fraction 2 (3.8 g) was filtered from the solution after prolonged storage. Fraction 3 was isolated from the remaining filtrate via precipitation with an equal volume of heptane, and fraction 4 was isolated from the liquid residue after evaporation of the solvent. The solid precipitate isolated from the cooled reaction mixture was extracted with boiling toluene; the solid residue was the fraction 1. The toluene solution was further processed as described above to yield additional amounts of the fractions 2–4. The fractions masses and the elemental compositions are given in the table.

ACKNOWLEDGMENTS

This work was financially supported by Ministry of Education and Science of the Russian Federation in the frame of the governmental contract (project 4.1517.2014/K).

REFERENCES

1. Voronkov, M.G., Maletina, E.A., and Roman, V.K., *Geteropolisiloksany* (Heteropolysiloxanes), Novosibirsk: Nauka, 1984.
2. Voronkov, M.G. and Khudobin, Yu.I., *Izv. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1956, no. 6, p. 713.
3. Voronkov, M.G. and Shapkin, N.P., *J. Organomet. Chem*., 1990, vol. 389, no. 2, p. 169. DOI: 10.1016/0022-328X(90)85409-R.
4. Kapustina, A.A., Shapkin, N.P., and Libanov, V.V., RF Patent 2483085, 2013.
5. Pliev, T.N., Zubkova, N.D., Turskii, Yu.I., and Dintses, A.I., *Vysokomol. Soed. (A),* 1969, vol. 11, no. 7, p. 1544.
6. Kapustina, A.A., Shapkin, N.P., Ivanova, E.B., and Lyakhina, A.A., *Russ. J. Gen. Chem*., 2005, vol. 75, no. 4, p. 571. DOI: 10.1007/s11176-005-0273-3.
7. Shapkin, N.P., Leont'ev, L.B., Leont'ev, A.L., Korochentsev, V.V., and Shkuratov, A.L., *Russ. J. Appl. Chem*., vol. 85, no. 10, p. 1509. DOI: 10.1134/S1070427212100035.
8. Shapkin, N.P., Alekhina, O.G., Reutov, V.A., Svistunova, I.V., and Vasilevskii, V.A., *Zh. Obshch. Khim*., 1992, vol. 62, no. 2, p. 505.
9. Shapkina, V.Ya., Medvedeva, V.B., and Shapkin, N.P., *Izv. Vuzov, Ser. Khim. Khim. Tekhnol*., 1988, vol. 31, no. 12, p. 119.
10. Shapkin, N.P., Leont'ev, L.B., Alekseiko, L.N., Pobozhev, K.V., and Gardionov, S.V., *Butlerov. Soobshch*., 2013, vol. 36, no. 10, p. 48.
11. Miller, R.L. and Boyer, R.F., *J. Polym. Sci*., 1984, vol. 22, p. 2043.
12. Shapkin, N.P., Razov, V.I., Voznesenskii, S.S., Bazhenov, V.V., Tutov, M.V., Stavnistyi, N.N., Kuryavyi, V.G., and Slobodyuk, A.B., *Russ. Chem. Bull*., 2011, vol. 60, no. 8, p. 1640. DOI: 10.1007/s11172-011-0245-1.
13. Kuz'mina, N.P., Chechernikova, M.V., and Martynenko, L.I., *Zh. Neorg. Khim*., 1990, vol. 35, no. 11, p. 2776.
14. Grove, D.E. and Johnson, N.F., *J. Chem. Soc*., 1965, vol. 1, p. 490.
15. Morozova, N.B., Zharkova, G.I., Stabnikov, P.A., Tyukalevskaya, N.M., Kradenov, K.V., Semyannikov, P.P., Tkachev, S.V., Potapova, O.G., and Igumenov, I.K., *Sintez i fiziko-khimicheskoe issledovanie β-diketonatov shchelochnozemel'nykh metallov* (Synthesis and Physico-Chemical Research of Earth Metal β-Diketonates), Preprint 89–08, Novosibirsk, 1989.
16. Andrianov, K.A. and Khananashvili, L.M., *Tekhnologiya elementoorganicheskikh monomerov i polimerov* (Technology of Organoelement Monomers and Polymers), Moscow: Khimiya, 1973.
17. Kapustina, A.A., Shapkin, N.P., and Libanov, V.V., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 7, p. 1320. DOI: 10.1134/S1070363214070123.