SYNTHESIS, POLYMERIZATION, AND COPOLYMERIZATION OF POLYORGANOSILOXANES CONTAINING METHACRYLATE GROUPS—I*

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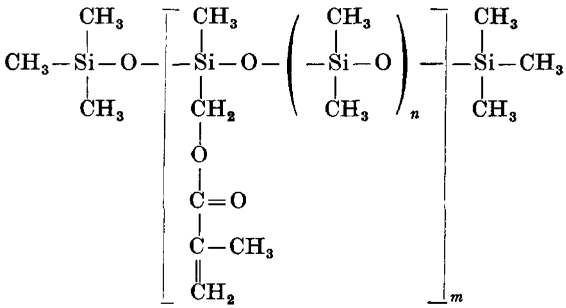
IN EARLIER investigations [1, 2] we have synthesized silicon-containing unsaturated polyethers and have studied their copolymerization with styrene. It was of interest to synthesize polyorganosiloxanes containing methacrylate groups as substituents on the silicon atoms and to study their polymerization and copolymerization with various vinyl compounds in order to elucidate the possibility of obtaining polymeric adhesives for reinforced plastics with a high heat stability.

Adrianov and Dabagova [3, 4] have shown that to obtain cross-linked polymers containing silicon it is possible to start from low-molecular-weight linear polyorganosiloxanes having terminal groups capable of polymerization (methacrylic, carboxyallyl groups).

In the present work, we have synthesized linear polyorganosiloxanes containing methacrylyloxymethyl groups as substituents on the silicon atoms, have studied their properties as functions of the frequency of occurrence of such groups along the molecule, and have carried out cross-linking and a thermomechanical investigation of the cross-linked polymers.

Poly-(methylmethacrylyloxymethyldimethylsiloxanes) of the general formula



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[-\underset{CH_2-O-C(=O)-C(CH_3)=CH_2}{\overset{CH_3}{Si}}-O-\left(-\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_n-\right]_m-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

were synthesized by the heterofunctional condensation of equivalent amounts of dimethyldiacetoxysilane and dimethyldiethoxysilane with a suitable predeter-

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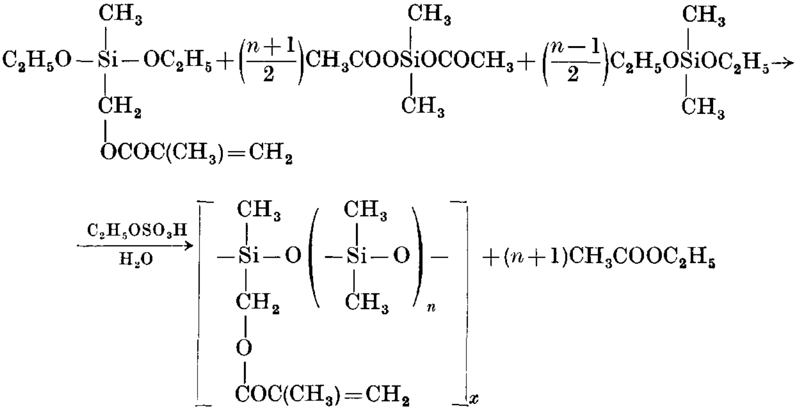
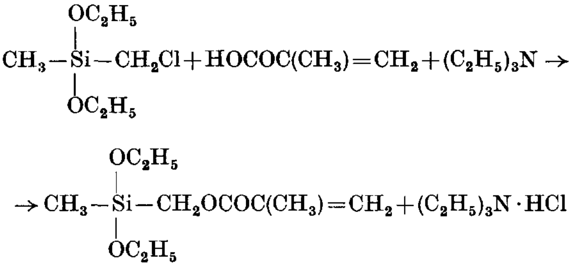
mined molar ratio of the latter component replaced by methylmethacrylyloxymethyldiethoxysilane.The reaction took place when the reaction mixture was kept at room temperature.



$$\mathrm{C_2H_5O-}\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{OCOC(CH_3)=CH_2}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{Si}}}\mathrm{-OC_2H_5}+\left(\frac{n+1}{2}\right)\mathrm{CH_3COO}\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{Si}}}\mathrm{OCOCH_3}+\left(\frac{n-1}{2}\right)\mathrm{C_2H_5O}\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{Si}}}\mathrm{OC_2H_5}\rightarrow$$

$$\xrightarrow[\mathrm{H_2O}]{\mathrm{C_2H_5OSO_3H}}\left[-\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{O}\\ |\\ \mathrm{COC(CH_3)=CH_2}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{Si}}}-\mathrm{O}\left(-\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{Si}}}-\mathrm{O}\right)_n-\right]_x+(n+1)\mathrm{CH_3COOC_2H_5}$$

The catalyst used was that recommended by Adrianov and Dabagova [4] — ethylsulphuric acid containing water in an amount of not less than 2% of the weight of the mixture of silanes. The methylmethacrylyloxymethyldiethoxysilane required for the reaction was obtained from the corresponding chloromethylsilane and methacrylic acid in the presence of triethylamine. The reaction of the chloromethylsilanes with methacrylic acid salts of organic bases

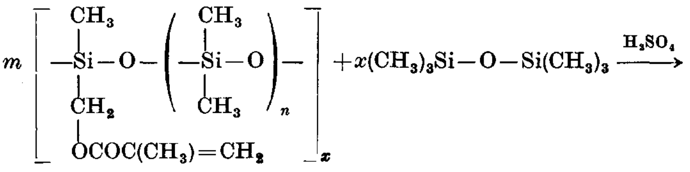


$$\mathrm{CH_3-}\underset{\substack{|\\ \mathrm{OC_2H_5}}}{\overset{\substack{\mathrm{OC_2H_5}\\ |}}{\mathrm{Si}}}\mathrm{-CH_2Cl+HOCOC(CH_3)=CH_2+(C_2H_5)_3N}\rightarrow$$

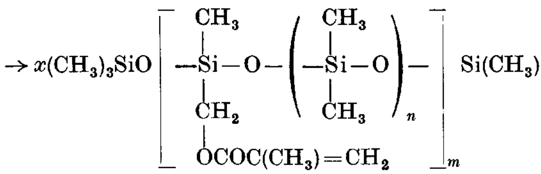
$$\rightarrow\mathrm{CH_3-}\underset{\substack{|\\ \mathrm{OC_2H_5}}}{\overset{\substack{\mathrm{OC_2H_5}\\ |}}{\mathrm{Si}}}\mathrm{-CH_2OCOC(CH_3)=CH_2+(C_2H_5)_3N\cdot HCl}$$

took place when the reactants were boiled in xylene solution with better yields than when the reaction was carried out with potassium methacrylate [4].

The condensation products were then treated with the calculated amount of hexamethyldisiloxane in the presence of concentrated sulphuric acid in order to obtain polyorganosiloxanes with a predetermined chain length. Rearrangement took place with the formation of linear polymeric molecules



$$m\left[-\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{OCOC(CH_3)=CH_2}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{Si}}}-\mathrm{O}-\left(-\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{Si}}}-\mathrm{O}\right)_n-\right]_x+x\mathrm{(CH_3)_3Si-O-Si(CH_3)_3}\xrightarrow{\mathrm{H_2SO_4}}$$



$$\rightarrow x(CH_3)_3SiO\left[-\underset{\underset{OCOC(CH_3)=CH_2}{|}}{\underset{CH_2}{\overset{CH_3}{Si}}}-O-\left(-\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_n-\right]_m Si(CH_3)_3$$

In this way we obtained the poly-(methylmethacrylyloxymethyldimethylsiloxanes) for which $n=0$, 1, 2, 3, 5, and 9 in the form of transparent colourless liquids. The analytic results were in good agreement with the theoretically calculated compositions (see Table 1). The molecular weights of the polymers, determined experimentally by the methods of isothermal distillation and cryoscopy, were somewhat low because of the possible presence of small amounts of low-molecular-weight impurities.

Figure 1 gives the density, refractive index, and kinematic viscosity as functions of the composition of the polysiloxanes. In order to exclude the influence of differences in the lengths of the polymeric molecules on the viscosity to some extent, ν/M is plotted along the axis of ordinates, where ν is the kinematic viscosity and M is the molecular weight of the polyorganosiloxane.

TABLE 1. CHARACTERISTICS OF THE POLYORGANOSILOXANES CONTAINING METHACRYLYLOXYMETHYL GROUPS SYNTHESIZED

R′: Si ratio*	Analysis, %						Mol. wt.	d_4^{20}	n_D^{20}	Kinematic viscosity, cSt
	C		H		Si					
	Found	Calculated	Found	Calculated	Found	Calculated				
1:1·05	45·62		6·61		18·19					
		45·60		6·58		18·25	2180	1·102	1·4680	163·0
	45·63		6·45		18·19					
1:2·11	41·32		7·01		23·91					
		41·51		7·06		24·50	2030	1·042	1·4483	94·8
	41·68		7·15		24·05					
1:3·17	40·23		7·63		27·50					
		39·50		7·36		27·75	1645	1·020	1·4372	66·6
	40·29		7·53		27·57					
1:4·22	38·40		7·62		30·11					
		38·20		7·54		29·72	2120	1·004	1·4312	68·8
	38·70		7·64		29·93					
1:6·33	37·14		7·74		31·89					
		36·75		7·75		31·95	1755	0·987	1·4233	44·0
	37·18		7·80		31·50					
1:10·3	35·09		8·06		33·44					
		35·50		7·95		34·10	2330	0·975	1·4178	57·6
	35·34		8·03		33·46					

* R′ – methacrylyloxymethyl group.

The specific gravities, refractive indices, and kinematic viscosities of the polyorganosiloxanes rise with an increase in the relative content of methacrylic groups in them. The influence of the methacrylic groups is shown relatively more clearly when their content is low.

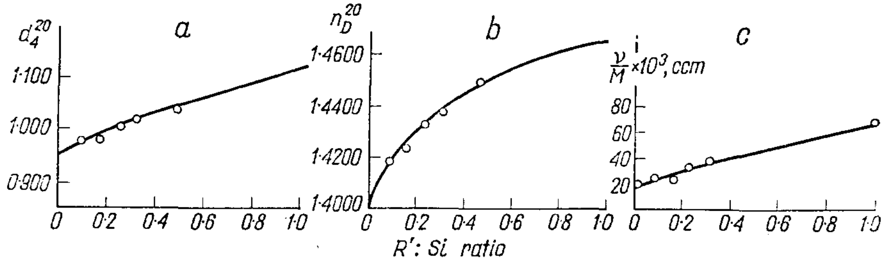


FIG. 1. Influence of the relative content of methacrylyloxymethyl groups in the polyorganosiloxanes on their properties: *a*—density; *b*—refractive index; *c*—kinematic viscosity; R′—methacrylyloxymethyl group.

All the polysiloxanes containing methacrylic groups are capable of polymerizing and of copolymerizing with other unsaturated organic monomers with the formation of cross-linked insoluble products. The polymers and copolymers with styrene of the polysiloxanes with a R′ : Si ratio of from 1 : 1 to 1 : 6 inclusive consist of solid colourless glasses. Figure 2 shows the deformation—temperature curve taken in a thermomechanical investigation of the polymer with a R′ : Si ratio of about 1 : 3. As can be seen from the Figure, the polymer has no melting point and does not pass into the elastic state before decomposition. Decomposition of the polymer begins at a temperature ~400°.

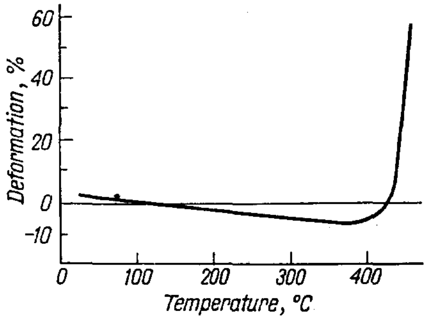


FIG. 2. Deformation curve of the polyorganosiloxane with a R′ : Si ratio ≈1 : 3.

The negative deformations on the curve (expansion) are associated with the high temperature coefficients of the expansion of the polyorganosiloxanes [5], as is also shown by the linear dependence of these deformations on the temperature.

EXPERIMENTAL

Starting materials. The triethylamine and methacrylic acid used were technical products purified by redistillation: the first at atmospheric pressure (b.p. 87–88°/743 mm); the second in vacuum in an atmosphere of nitrogen in the presence of hydroquinone and powdered copper (b.p. 64–65°/11 mm). The chloromethylmethyldiethoxysilane was obtained by chlorinating dimethyldichlorosilane in a Kursanov apparatus by a known method [6] with subsequent esterification with absolute ethyl alcohol; the product had b.p. 160–162°/ /737 mm, n_D^{20} 1·4163 (according to literature data: b.p. 160–163°, n_D^{20} 1·4150 [7]).

Dimethyldiethoxysilane (b.p. 113–114·5°; n_D^{20} 1·3838) and dimethyldiacetoxysilane (b.p. 155–162°; n_D^{20} 1·4020) were obtained by known methods from dimethyldichlorosilane and absolute ethyl alcohol and from dimethyldichlorosilane and acetic anhydride [8].

Methacrylyloxymethylmethyldiethoxysilane. A flask fitted with a reflux condenser was charged with 200 ml of dry xylene, 121·5 g (0·665 mole) of chloromethylmethyldiethoxysilane, 69·4 g (0·8 mole) of methacrylic acid, 74·0 g (0·73 mole) of triethylamine, and 3·5 g of hydroquinone. The mixture was heated to the boil for 4 hours. After cooling, the precipitate of triethylamine hydrochloride was filtered off and washed on the filter twice with small portions of xylene; the yield of hydrochloride was 100%. The filtrate was treated with 2 g of powdered copper and 1 g of hydroquinone and subjected to distillation. In vacuum, 85 g of a fraction with b.p. 80–82°/3 mm was isolated. On redistillation, the product boiled at 79–81°/2·5 mm, n_D^{20} 1·4283; according to literature data: b.p. 97–98°/5 mm, n_D^{20} 1·4260 131; yield 53·0% of theoretical.

TABLE 2. COMPOSITIONS OF THE REACTION MIXTURES AND YIELDS OF THE REACTION PRODUCTS

R′:Si ratio	Composition of the reaction mixture, g				Yield of condensation products, g (%)	Added hexamethyldisiloxane, g	Yield of products after rearrangement, g (%)
	Methacrylyloxymethylmethyldiethoxysilane	Dimethyldiethoxysilane	Dimethyldiacetoxysilane	Molar ratio			
1:1·05	20·6	—	—	—	12·25 (87·5)	0·39	10·75 (85·2)
1:2·11	18·56	—	14·08	1:0:1	16·33 (88·0)	0·63	14·00 (82·7)
1:3·17	18·65	5·95	21·17	2:1:3	20·00 (82·0)	0·88	17·85 (85·5)
1:4·22	11·6	7·40	17·60	1:1:2	15·63 (83·0)	0·74	—
1:6·33	6·96	8·88	15·84	1:2:3	13·0 (82·3)	0·66	12·74 (93·0)
1:10·3	7·00	17·20	26·40	1:4:5	21·25 (87·7)	1·10	20·35 (91·5)

Poly-(methylmethacrylyloxymethyldimethylsiloxane)s. A flask fitted with a dropping funnel and an electromagnetic stirrer was charged with a mixture of 11·6 g (0·05 mole) of methacrylyloxymethylmethyldiethoxysilane, 7·4 g (0·05 mole) of dimethyldiethoxysilane, and 17·6 g (0·10 mole) of dimethyldiacetoxysilane and, with stirring and external cooling of the flask with ice-water, 3·6 g (10% of the weight of the silanes) of aqueous ethylsulphuric acid (obtained by mixing 23·8 g of conc. sulphuric acid, 11·6 g of ethyl alcohol, and 16·5 g of water) was added in drops. The mixture was allowed to stand at room temperature for 2 days, after which the upper layer was separated, washed with sodium bicarbonate solution and water, and dried with anhydrous magnesium sulphate, and the ethyl acetate was distilled off in vacuum (during this, the temperature of the water bath did not exceed 40–45 °). This gave a residue of 15·63 g of viscous liquid to which was added 0·74 g of hexamethyldisiloxane and then, with ice-water cooling and stirring, 1·5 ml of conc. H_2SO_4. After a day, 3 ml of water was added to the mixture and it was then stirred for 1 hour, diluted with an approximately equal volume of methylene chloride and washed with water, sodium bicarbonate solution, and water again. After drying, the solvent was distilled off in vacuum (2 mm, bath temperature $\leqslant 40$ °) with the passage of a current of nitrogen to give a colourless viscous liquid—a polysiloxane with a R′ : Si ratio of 1 : 4. The other poly-(methacrylyloxymethyldimethylsiloxane)s the properties of which are given in Table 1 were obtained in a similar manner, but with the different ratios of the initial silanes given in Table 2.

Poly-(methylmethacryloxymethylsiloxane). A polysiloxane containing methacrylic groups on each silicon atom was obtained when, in contrast to the other polysiloxanes, instead of the heterofunctional condensation of ethoxysilanes with acetoxysilanes, hydrolysis of methacrylyloxymethylmethyldiethoxysilane was carried out with a mixture of water and alcohol in the presence of sulphuric acid. The properties of the product obtained are given in Table 1 (R′ : Si = 1 : 1·05).

CONCLUSIONS

(1) Methacrylyloxymethylmethyldiethoxysilane has been obtained in good yield by the reaction of chloromethylmethyldiethoxysilane with methacrylic acid and triethylamine.

(2) Linear polyorganosiloxanes containing methacrylyloxymethyl groups on the silicon atoms in different ratios have been synthesized by heterofunctional condensation.

(3) The densities, refractive indices, and kinematic viscosities of the polyorganosiloxanes rise with an increase in the content of methacrylyloxymethyl groups in them.

(4) Polyorganosiloxanes containing methacrylyloxymethyl groups polymerize and copolymerize with other unsaturated compounds in the presence of peroxides to form solid glass-like products. The decomposition temperature of the cross-linked three-dimensional polymers determined from the thermomechanical curves, is in the region of 400–420°.

Translated by B. J. HAZZARD

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