

## Methacrylate Compositions Modified by Oligosilsesquioxanes with Methacryl and Cyclotriphosphazene Substituents

N. S. Bredov<sup>a,\*</sup>, E. Yu. Shporta<sup>a</sup>, M. V. Gorlov<sup>a</sup>, V. V. Kireev<sup>a</sup>,  
S. N. Filatov<sup>a</sup>, V. F. Posokhova<sup>b</sup>, and V. P. Chuev<sup>b</sup>

<sup>a</sup> Mendeleev University of Chemical Technology, Miusskaya pl. 9, Moscow, 125047 Russia

<sup>b</sup> ZAO VladMiVa, ul. Michurina 39a, Belgorod, 308002 Russia

\*e-mail: koljabs@rambler.ru

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**Abstract**—Triethoxysilylphosphazenes have been synthesized via hydrosilylation of cyclotriphosphazenes with various contents of 4-allyl-2-methoxyphenoxy groups by triethoxysilane at an equimolar phosphazene–silane ratio. Hydrolytic copolycondensation of the latter compounds with  $\gamma$ -methacryloxypropyltrimethoxysilane resulted in oligosiloxanes involving functional methacrylic and phosphazene fragments. The oligomers have been used as additives to a dental composition based on bisphenol A-diglycidyl methacrylate and triethylene glycol dimethacrylate. The modified filled compositions are characterized by reduced (4-fold) sensitivity to external illumination and improved strength properties and microhardness.

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As is known, it is possible to synthesize oligosilsesquioxanes via hydrolytic or acidhydrolytic polycondensation of trialkoxysilanes [1, 2]. During copolycondensation of various alkoxy silanes, for example, those containing methacrylic and cyclotriphosphazene fragments, silsesquioxane oligomers promising as modifiers of polymer compositions for medical use (particularly in orthopedics and dentistry) may be obtained.

An efficient method of synthesis of trialkoxysilanes with phosphazene fragments is the catalytic hydrosilylation of unsaturated aliphatic groups in organic substituents of cyclophosphazene with trialkoxysilane hydrides [3].

The aim of this study was to show the possibility to obtain methacrylate-containing oligosilsesquioxanes with cyclotriphosphazene substituents in side radicals.

### EXPERIMENTAL

As initial organophosphazenes, eugenol derivatives of hexachlorocyclotriphosphazene (HCP) were chosen. The first product, a mixture of tris(4-allyl-2-methoxyphenoxy)trichlorocyclotriphosphazenes (TEPs), was prepared as described in [3]; according to the data of <sup>31</sup>P NMR spectroscopy, it involves 77 wt % nongeminally substituted cis isomer, 15 wt % nongeminal trans isomer, and 8 wt % geminal TEP. Hereafter, this mixture was used without separation into individual compounds.

The second product, synthesized via a method described previously [4], comprised 77 wt % penta-(4-allyl-2-methoxyphenoxy)cyclotriphosphazene (PEP)

and 23 wt % hexa-(4-allyl-2-methoxyphenoxy)cyclotriphosphazene (HEP).

<sup>1</sup>H NMR spectra of the initial eugenol cyclotriphosphazenes display identical proton chemical shifts:  $\delta$  3.2–3.3 (d, Ar–CH<sub>2</sub>–CH=), 3.6–3.8 (s, Ar–OCH<sub>3</sub>), 5.0–5.1 (d, CH<sub>2</sub>–CH=CH<sub>2</sub>), 5.9–6.0 (m, CH<sub>2</sub>–CH=CH<sub>2</sub>), 6.5–7.0 (m, protons of aromatic cycles) ppm. Because, in eugenoxycyclotriphosphazenes, compounds with various degrees of substitution or isomers are present, the proton signals are broadened owing to various environments of phosphorus atoms and, hence, their shielding.

Triethoxysilane (ABCR, 97% basic compound,  $T_b = 131–132^\circ\text{C}$ ) was used without further purification.

$\gamma$ -Methacryloxypropyltrimethoxysilane (A-174, Acros, 98% basic compound,  $T_b = 190^\circ\text{C}$ ,  $n_D^{25} = 1.432$ ) was used without further purification. <sup>29</sup>Si NMR (CDCl<sub>3</sub>):  $\delta$  –43.5 (s) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.49 (t, –CH<sub>2</sub>–Si), 1.55 (m, –CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–), 1.75 (s, CH<sub>3</sub>C), 3.35 (s, CH<sub>3</sub>O–), 3.88 (t, –CH<sub>2</sub>O–), 5.30 and 5.85 (2 s, C=CH<sub>2</sub>) ppm.

Hydrosilylation of eugenol derivatives of cyclotriphosphazenes by triethoxysilane (for the example of trieugenol derivatives of hexachlorocyclotriphosphazene) was performed in a three-neck flask equipped with a stirrer, a reflux, and a thermometer. Into the flask, toluene (28.6 g), TEP (10 g), Karstedt's catalyst (0.184 mg), and triethoxysilane (2.25 g) were successively charged. The synthesis was performed under constant stirring in three stages for 4 h at 60, 70, and 80°C. Once the solvent was removed, 11.6 g of a trans-

parent light yellow viscous liquid was obtained. The hydrosilylation of a mixture of penta- and hexaegenol derivatives of HCP was performed in a similar manner.

Hydrolytic copolycondensation of triethoxysilylphosphazenes with  $\gamma$ -methacryloxypropyltrimethoxysilane was conducted in a three-neck flask with a stirrer under reflux. Into the flask, A-174 (3.6 g) and the product of TEP hydrosilylation by triethoxysilane (13 g) were charged and dissolved in THF (355 mL) at a molar ratio of triethoxysilylphosphazene : A-174 = 1 : 1. To the reaction mixture, 36% HCl (0.47 g) and water (1.26 g) were added. The process was carried out at 50°C for 30 h under constant stirring. Once the process was completed, the reaction mixture was precipitated in a 10% NaCl aqueous solution. The resulting precipitate was separated, dissolved in chloroform, and repeatedly washed with water. Then, the solution was dried with MgSO<sub>4</sub>, the solvent was removed on a rotary vacuum evaporator, and the product was dried

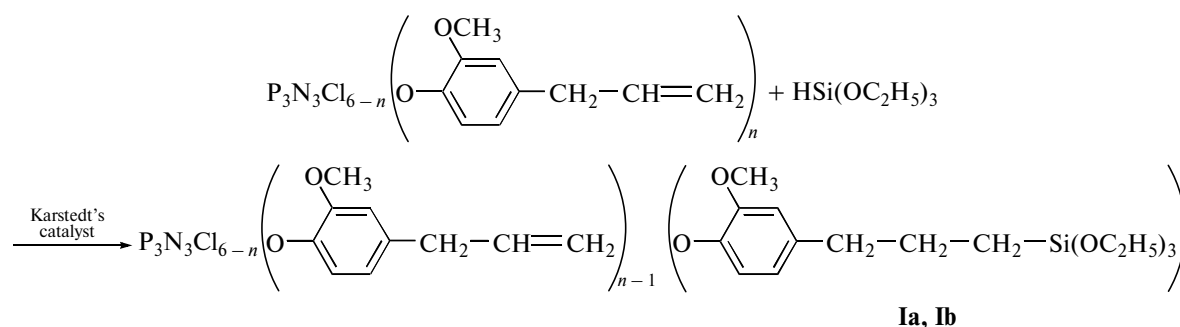
under vacuum. A light yellow viscous oligomer product (13.75 g) was obtained. Copolycondensation of a mixture of penta- and hexasubstituted HCPs was performed in a similar manner.

<sup>1</sup>H, <sup>31</sup>P, and <sup>29</sup>Si NMR spectra were recorded on Bruker CXP-200 and Bruker AMX-360 spectrometers at 25°C in a deuteriochloroform solution.

The molecular masses of oligosilsesquioxanes were determined via GPC on a Waters chromatograph (Styragel columns, a UV detector, THF as an eluent, an elution rate of 1 mL/min).

## RESULTS AND DISCUSSION

Hydrosilylation of mixtures of HCP eugenol derivatives was performed in a 30% toluene solution in the presence of Karstedt's catalyst at an equimolar triethoxysilane-to-cyclotriphosphazene ratio



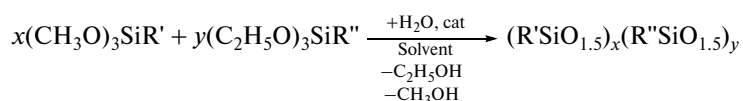
where **Ia** is formed at  $n = 3$  and **Ib** is formed at  $n = 5$  and 6.

<sup>1</sup>H NMR spectra of the products of hydrosilylation of mixtures of HCP eugenol derivatives **Ia** and **Ib** with triethoxysilane display proton signals in the region of 1.2 and 3.7 ppm due to the groups  $-\text{OCH}_2-$  and  $\text{Si}-\text{OCH}_2-\text{CH}_3$ , respectively, as well as signals of protons of the methylene chain at 2.6, 1.75, and 0.7 ppm due to the groups  $\text{Ar}-\text{CH}_2-$ ,  $\text{Ar}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ , and  $\text{CH}_2-\text{CH}_2-\text{Si}$ , respectively (Fig. 1). The integral intensities of the corresponding signals in the <sup>1</sup>H

NMR spectra of hydrosilylation products are indicative of the quantitative addition of triethoxysilane fragments.

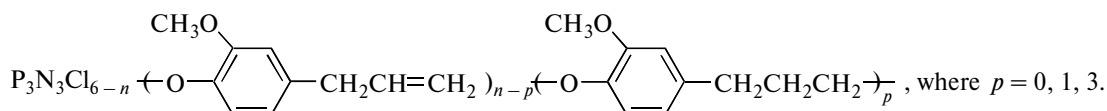
<sup>31</sup>P NMR spectra of hydrosilylation products **Ia** and **Ib** exhibit a set of signals characteristic of the initial HCP eugenol derivatives.

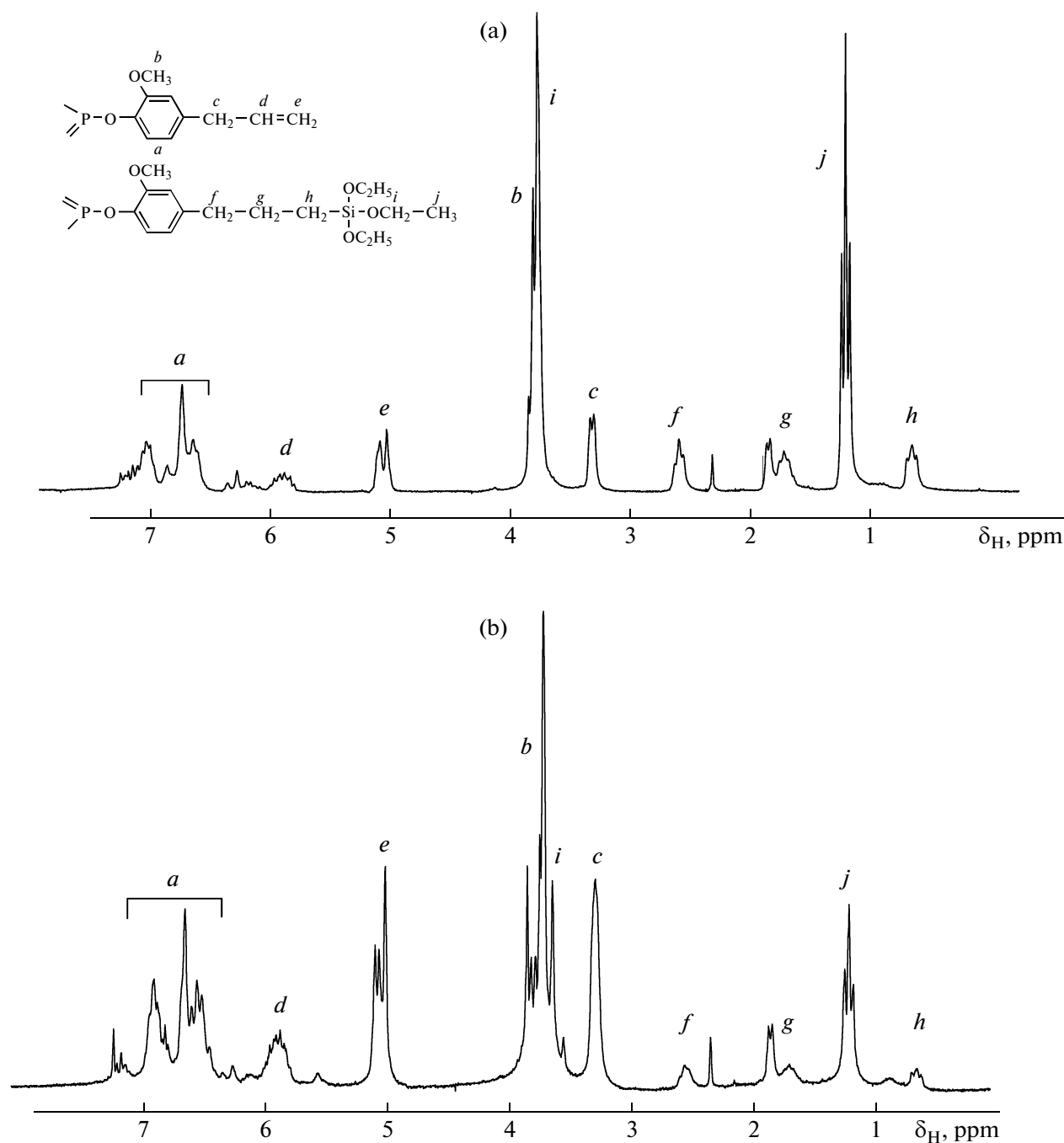
Hydrolytic copolycondensation of **Ia** or **Ib** with A-174 was performed under homogeneous conditions in THF (3 mol water/1 mol silanes) in the presence of a catalytic amount of HCl according to the following scheme.



Here  $\text{R}' = -(\text{CH}_2)_3-\text{O}-\text{C}(\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$  (monomer A-174);

$\text{R}''$  is a cyclotriphosphazene radical of the general formula

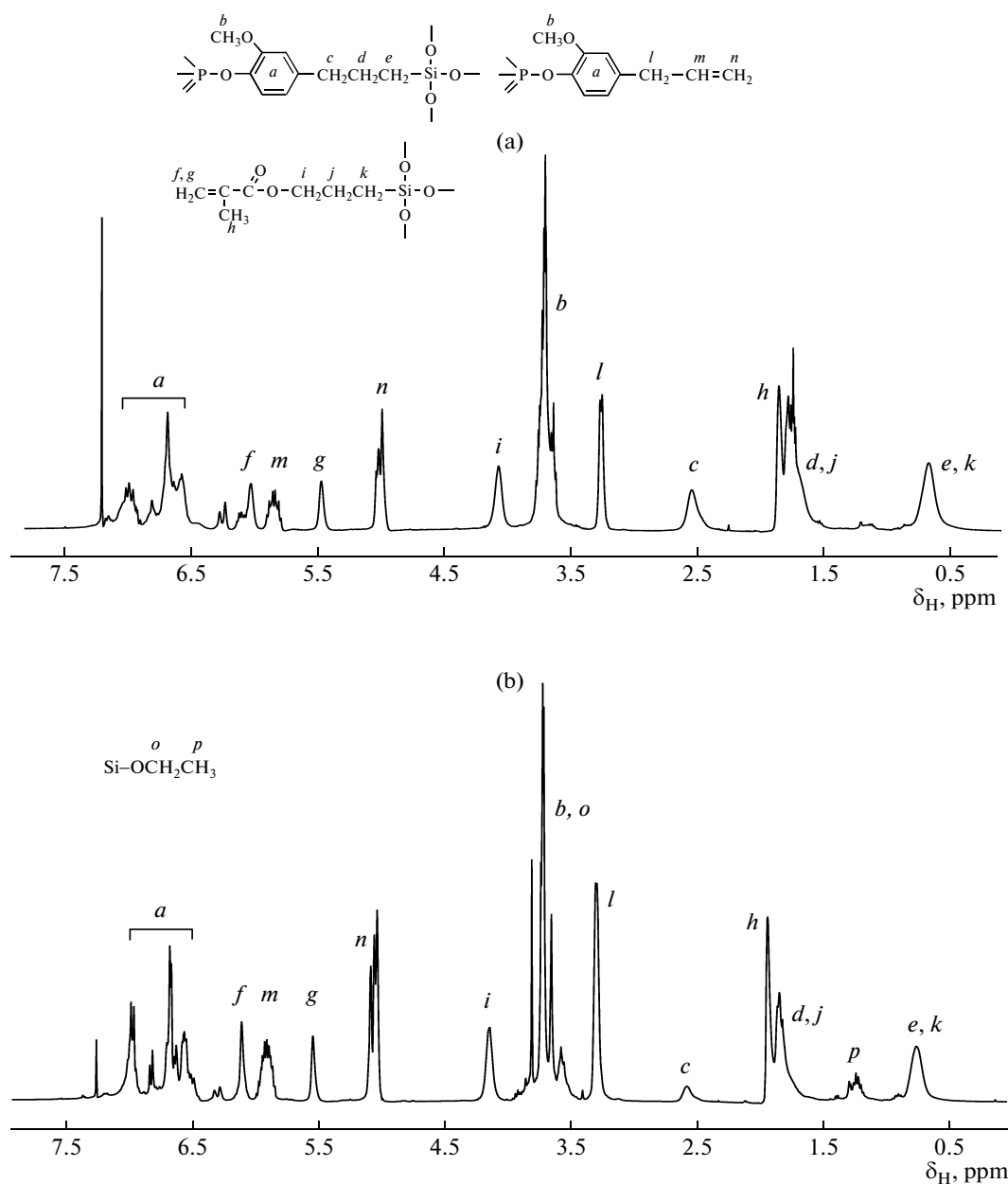




**Fig. 1.**  $^1\text{H}$  NMR spectra of hydrosilylation products (a) Ia and (b) Ib. The molar ratios are A-174 : Ia = 1 : 1 and A-174 : Ib = 2 : 1.

On the basis of the data of  $^1\text{H}$  NMR spectroscopy (Fig. 2), in spite of the quantitative hydrolytic splitting out of alkoxy groups in the initial silanes at a silane-to-water molar ratio of 1 : 3, the subsequent silanol polycondensation, as should be expected, was not complete. According to the data of  $^{29}\text{Si}$  NMR spectra (Fig. 3), the products of cohydrolysis of **Ia** and A-174 involved 5–10%  $-\text{RSi}(\text{OH})_2\text{O}_{0.5}-$  units on average (here and hereinafter, R is R' or R''), 25–30%

$\text{RSi}(\text{OH})\text{O}(\text{units})$ , and 55–65% silsesquioxane fragments  $\text{RSiO}_{1.5}-$ . The  $^{29}\text{Si}$  NMR spectrum of the product of cohydrolysis of **Ib** and A-174 is similar to that shown in Fig. 3. The GPC curves of phosphazenesiloxane oligomers are unimodal (Fig. 4), a circumstance that confirms the absence of separate condensation of silanol groups of products of hydrolysis of A-174 and ethoxysilylphosphazenes. For phosphazenesiloxane oligomers,  $M_n$  is  $(3-5) \times 10^3$  and  $M_w$  is  $(19-$



**Fig. 2.**  $^1\text{H}$  NMR spectra of the products of hydrolytic copolycondensation of A-174 with (a) Ia and (b) Ib. The molar ratios are A-174 : Ia = 1 : 1 and A-174 : Ib = 2 : 1.

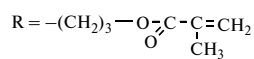
$35) \times 10^3$  (Table 1); all the products were transparent viscous resinous masses well compatible with methacrylic monomers and oligomers.

The synthesized hybrid siloxanephosphazenes (HSPs) were tested as modifiers of dental filling compositions based on a filled mixture of 2,2-bis[*p*-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane (bis-HMA) and triethylene glycol dimethacrylate (TGM-3) (Table 2).

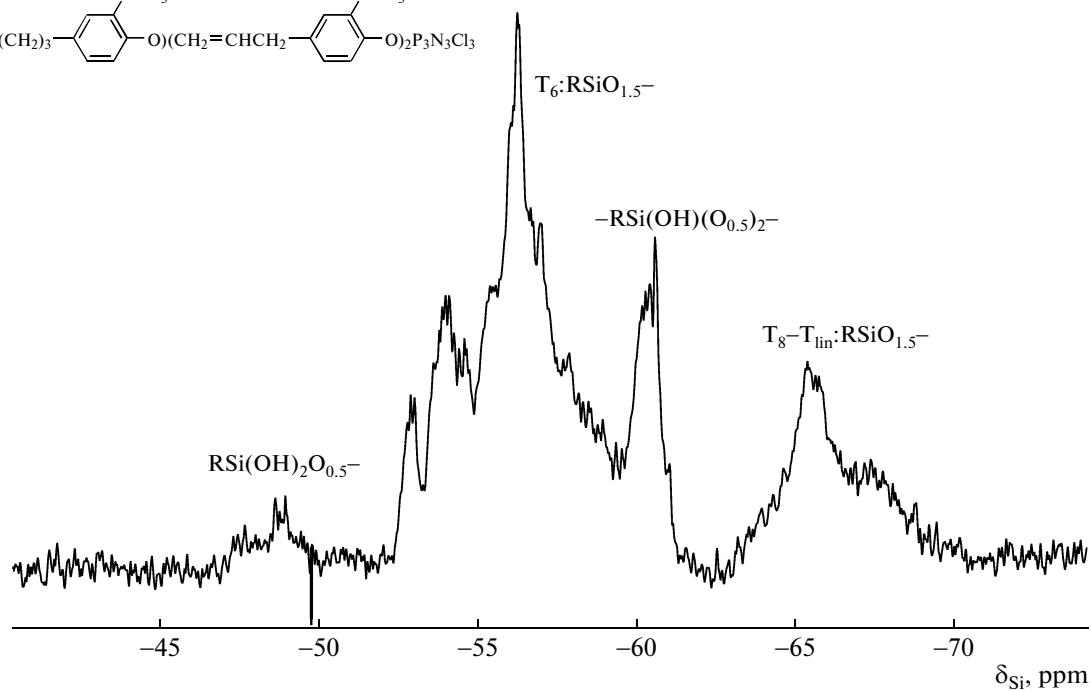
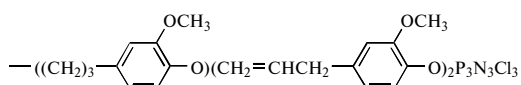
Thus, the addition of 10–15 wt % HSP results in improved mechanical characteristics of cured compositions along with a simultaneous significant (a four-

fold) decrease in the sensitivity to external illumination, a result that is positive for dental filling compositions. In terms of this factor, the most efficient was the HSP-1 sample, although the mechanical characteristics increase significantly during the use of the HSP-3 modifier.

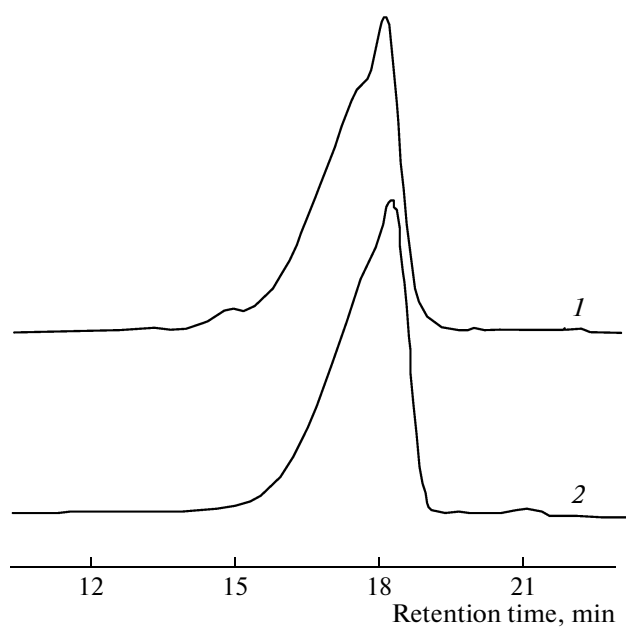
The subsequent introduction of P–OH and P=O groups formed during hydrolysis of residual chlorine atoms in HSP into a cyclotriphosphazene fragment of the hybrid siloxanephosphazene oligomer suggests significant increases in both the strength and adhesion characteristics of the dental filling composite.



or



**Fig. 3.**  $^{29}\text{Si}$  NMR spectrum of the product of hydrolytic copolycondensation of A-174 with Ia. The molar ratio is A-174 : Ia = 1 : 1.



**Fig. 4.** GPC curves of the products of hydrolytic copolycondensation of A-174 with Ia. The molar ratios are A-174 : Ia = (1) 1 : 1 and (2) 2 : 1.

**Table 1.** Ratios of the initial comonomers and molecular-mass characteristics of the resulting HSPs

Sample no.	Initial phosphazene-containing ethoxysilane	Molar ratio A-174 : Ia or A-174 : Ib	Content*, %				$M \times 10^{-2}$ (GPC)	
			Cl	N	P	Methacryl groups**	$M_n$	$M_w$
HSP-1	Ib	2 : 1	$\frac{2.08}{1.74}$	$\frac{2.22}{2.69}$	$\frac{5.57}{5.95}$	14.2	55	350
HSP-2	Ia	1 : 1	$\frac{11.73}{11.11}$	$\frac{3.58}{4.39}$	$\frac{9.12}{9.70}$	8.6	35	190
HSP-3	Ia	2 : 1	$\frac{9.95}{9.60}$	$\frac{3.07}{3.79}$	$\frac{7.84}{8.38}$	13.9	32	220

\* The found value is in the numerator; the calculated value, in the denominator.

\*\* According to the data of  $^1\text{H}$  NMR spectra.

**Table 2.** Mechanical characteristics\* of filled cured compositions\*\* modified by HSP

Content of HSP sample, wt %	Ultimate stress, MPa			Elastic modulus, GPa	Microhardness, kg/mm <sup>2</sup>	Sensitivity to external illumination, s
	compression stress	bending stress	diametric-compression stress			
Modifier HSP-1						
0	278.0 ± 6.1	120.5 ± 2.8	38.4	9.8 ± 0.9	92.3 ± 1.2	35.0 ± 1.0
5	282.0 ± 5.6	121.6 ± 2.6	43.2	9.9 ± 0.7	96.5 ± 1.2	150.0 ± 1.0
10	288.6 ± 4.8	128.4 ± 2.4	45.3	10.1 ± 0.6	103.2 ± 1.4	160.0 ± 1.0
15	290.3 ± 3.8	129.7 ± 3.4	46.0	10.0 ± 0.4	104.6 ± 1.6	149.0 ± 1.0
20	275.6 ± 4.9	123.9 ± 2.3	45.4	9.8 ± 0.3	102.3 ± 1.1	137.0 ± 1.0
Modifier HSP-2						
5	298.2 ± 5.3	122.5	49.9	10.1 ± 0.6	97.3 ± 1.3	120.0 ± 1.0
10	303.3 ± 4.9	129.7	44.2	10.6 ± 0.6	104.9 ± 1.5	135.0 ± 1.0
15	304.2 ± 2.8	130.0	45.9	10.4 ± 0.5	105.8 ± 1.3	138.0 ± 1.0
20	286.3 ± 4.7	126.3	43.8	10.0 ± 0.4	103.8 ± 1.4	125.8 ± 1.0
Modifier HSP-3						
5	310.0 ± 5.2	123.4 ± 2.7	44.9	10.4 ± 0.8	98.4 ± 1.2	85.2 ± 1.0
10	335.0 ± 4.9	130.6 ± 2.5	46.2	10.5 ± 0.7	105.4 ± 1.3	90.0 ± 1.0
15	337.0 ± 5.0	131.8 ± 3.0	47.5	10.2 ± 0.3	106.3 ± 1.5	92.3 ± 1.0
20	320.0 ± 4.8	125.6 ± 2.6	46.3	10.6 ± 0.4	104.6 ± 1.2	91.9 ± 1.0

\* Tests were performed in compliance with ISO 4049-88, 10477-92, 11405-94.

\*\* Basic blend composition (wt fractions): filler, 77.0; bis(HMA) : TGM-3 = 7 : 3 (wt/wt), 23.0.

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