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RESEARCH ARTICLE

New polycarbonate siloxanes based on siloxane-*N*-phthalimidines

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Abstract

Objectives. *Polymeric carbonate siloxanes containing a siloxane-N-phthalimidine group in the chain frame are new synthetic comb-like macromolecule systems. This work aims to study the possibility of applying them in the form of film materials for heat-resistant, high-performance gas-permeable membranes.*

Methods. *Comb-like polycarbonate siloxanes of the siloxane-containing polyether class were obtained using various polycondensation methods, i.e., by the polymer-analogous transformation of polycarbonate-allyl-N-phthalimidines, using their reaction in an alkyl hydride siloxane solution; polycondensation of N-(3-(pentamethyldisiloxane)-propyl)-3,3-bis-(4'-hydroxyphenyl)-phthalimidine with diphenylolpropane bis-chloroformate in a solution using triethylamine as an acceptor of hydrochloric acid; interphase polycondensation of the above reagents in a dichloromethane aqueous alkali system. The structures of the obtained initial and polymeric compounds were confirmed by proton nuclear magnetic resonance spectroscopy and elemental analysis. All of the synthesized comb-like copolymers had good solubility in several available solvents and film formations.*

Results. *The new comb-like polycarbonate siloxanes had high thermal stability. According to thermogravimetric analysis, the introduction of up to 20 wt % siloxane units makes it possible to increase the heat resistance of polycarbonate siloxanes by 25°C. Concurrently, their glass-transition temperature reaches 160°C. Copolymers of polycarbonate siloxanes in the form of films have a high tensile strength above 50 MPa and an elastic modulus of up to 2000 MPa. The permeability coefficients of gases through a copolymer of polycarbonate siloxanes in the form of a film for several gases surpass the permeability of industrial polycarbonate from diphenylolpropane and fluorine-containing siloxane polycarbonate.*

Conclusions. *The results achieved indicate the possibility of creating new polymeric comb-shaped siloxane systems with a variable structure that can contribute to obtaining the properties desired from them. Combined with high selectivity gas separation, this makes it possible to use such comb-shaped polycarbonate siloxanes as film membrane materials with an increased operating temperature range.*

Keywords: *polycarbonate siloxanes, comb-like polymers, polycondensation, mechanical and thermal properties, gas permeability*

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НАУЧНАЯ СТАТЬЯ

Новые поликарбонатсилоксаны на основе силоксан-*N*-фталимидинов

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Аннотация

Цели. *Полимерные карбонатсилоксаны, содержащие в обрамлении цепи силоксан-N-фталимидиновую группировку, являются новыми синтетическими гребнеобразными системами макромолекул. Цель работы – изучить возможность их применения в виде пленочных материалов для термостойких высокоэффективных газопроницаемых мембран.*
Методы. *Гребнеобразные поликарбонатсилоксаны класса силоксан-содержащих полиэфиров были получены различными поликонденсационными методами: полимераналогичным превращением поликарбонат-аллил-N-фталимидинов их реакцией в растворе с алкилгидридсилоксанами; поликонденсацией N-(3-(пентаметилдисилокси)-пропил)-3,3-бис-(4'-окси-фенил)фталимидина с бис-хлорформиатом дифенилолпропана в растворе, используя триэтиламин в качестве акцептора соляной кислоты или межфазной поликонденсацией указанных реагентов в системе метиленхлорид–водная щелочь. Структуры полученных исходных и полимерных соединений были подтверждены спектроскопией ядерного магнитного резонанса ^1H и элементным анализом. Свойством всех синтезированных гребнеобразных сополимеров является их хорошая растворимость в ряде доступных растворителях и пленкообразование.*
Результаты. *Показано, что новые гребнеобразные поликарбонатсилоксаны обладают высокой термической устойчивостью. По данным термогравиметрического анализа введение в сополимер до 20 масс. % силоксановых звеньев позволяет повысить термостойкость поликарбонатсилоксанов на 25°C. При этом, температура стеклования их достигает 160°C. Сополимеры поликарбонатсилоксанов в виде пленок обладают высокой прочностью на разрыв выше 50 МПа и модулем упругости до 2000 МПа. Коэффициенты проницаемости газов через сополимер поликарбонатсилоксанов в виде пленки по ряду газов превосходят проницаемость для промышленного поликарбоната из дифенилолпропана и фторсодержащего силоксанового поликарбоната.*
Выводы. *Достигнутые результаты свидетельствуют о возможности создания новых полимерных гребнеобразных силоксановых систем с варьируемой структурой, которая способствует для них получению заданных свойств. В сочетании с высокой селективностью разделения газов это позволяет использовать новые гребнеобразные поликарбонатсилоксаны в качестве пленочных мембранных материалов с повышенным интервалом рабочих температур.*

Ключевые слова: *поликарбонатсилоксаны, гребнеобразные полимеры, поликонденсация, механические и термические свойства, газопроницаемость*

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INTRODUCTION

Polycarbonate siloxanes (PCS) have been broadly studied. Among these studies, in organosilicon copolymers, linear polycondensation polymers are important for practical purposes [1–4]. These are distinguished by high thermal stability, good mechanical properties, and high gas permeability.[1] Concurrently, the possibility of improving the service properties of PCS for their use as membrane materials may arise when changing not only their composition but also their molecular structure, i.e., when passing from linear copolymers of the $–(A–B)_n–$ type to comb-like structures of the $–[A(B)]_n–$type.

Such a structural approach to the creation of highly efficient gas-permeable membranes was implemented using the example of comb-shaped polystyrene siloxanes [5, 6]. The authors found that the presence of siloxane groups in polystyrene suspensions broadly changed the permeability selectivity of such polymers in terms of the O_2/N_2 gas pair in a range from 2.7 to 4.0. Hence, it was concluded that the structural and chemical factors of lateral siloxane branches affecting the packing and mobility of polymer chains play a decisive role in diffusion processes.

To date, there is a lack of publications related to polyether–polysiloxanes with comb-like structures. In our opinion, silicon phenols based on a phenolphthalein derivative with a grafted siloxane group are suitable as starting monomers for the production of comb-shaped polyesters and PCS using the polycondensation method [7, 8].

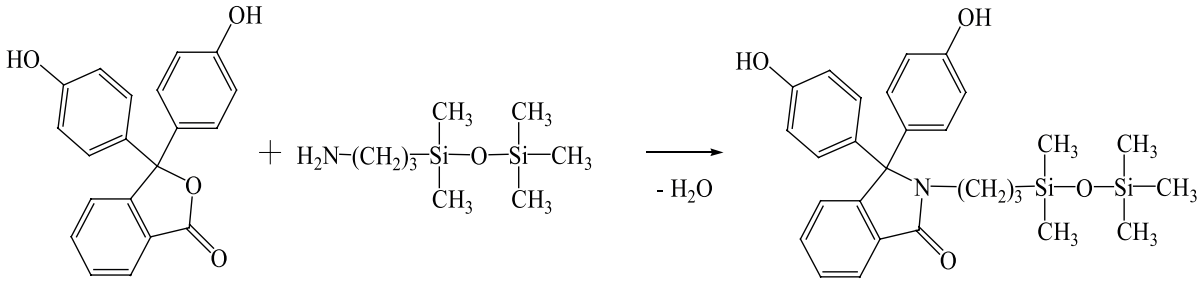
When synthesizing such bis-phenols, it was found [7] that the interaction of phenolphthalein with γ-aminopropylorganosiloxane proceeds according to the classic reaction, i.e., the preparation of siloxane-containing imidine bisphenols (Scheme 1).

However, according to gas–liquid and preparative high-performance liquid chromatography data, this reaction results in an entire range of different products (Scheme 2).

Synthesis excluding the Si–O–Si bond rearrangement, and creating only bis-phenols with a grafted siloxanephthalimidine group, was carried out according to Scheme 3 from *N*-allyl-3,3-bis-(4'-hydroxyphenyl) phthalimidine and monohydridesiloxanes [9].

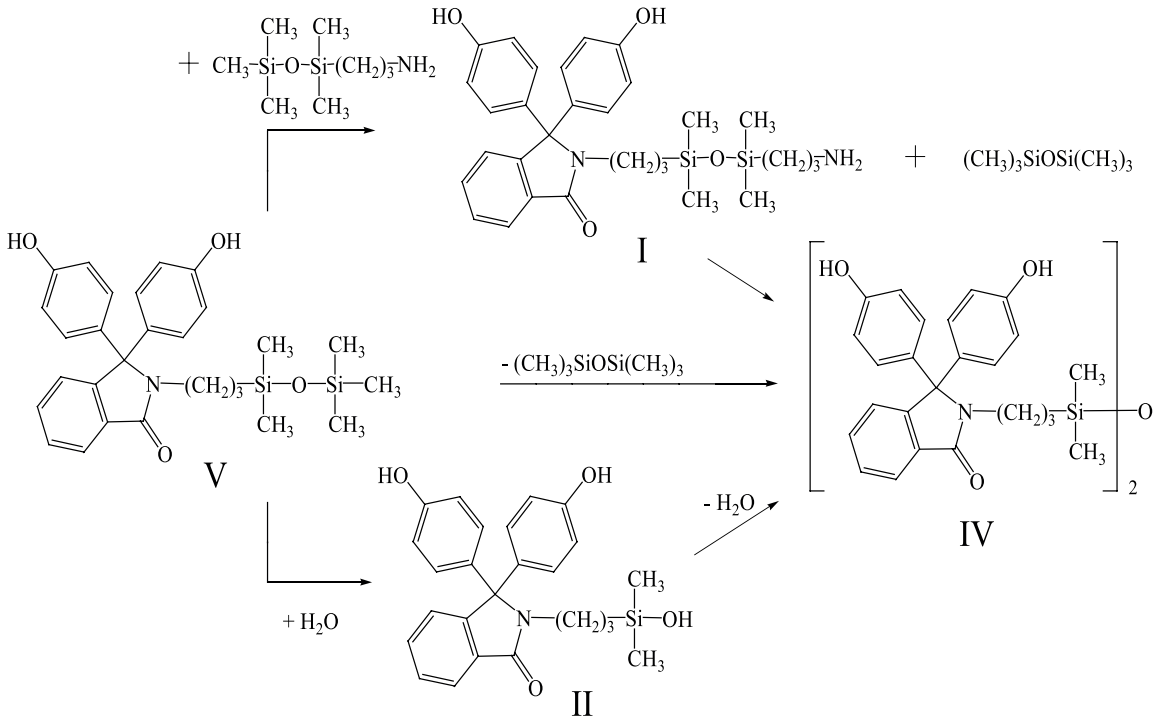
MATERIALS AND METHODS

We used *N*-allyl-3,3-bis-(4'-hydroxyphenyl)-phthalimidine obtained by the method developed by S.N. Salazkin.[2] The chemical purity of *N*-allylphthal-imidine after recrystallization (mp = 264–265°C) estimated by proton nuclear magnetic resonance (^{1}H NMR) was higher than 98 wt %. Monohydridesilanes: penta-methyldisiloxane hydride and heptamethyltrisiloxane hydride (98%, *Penta*, Russia); dichloromethane,

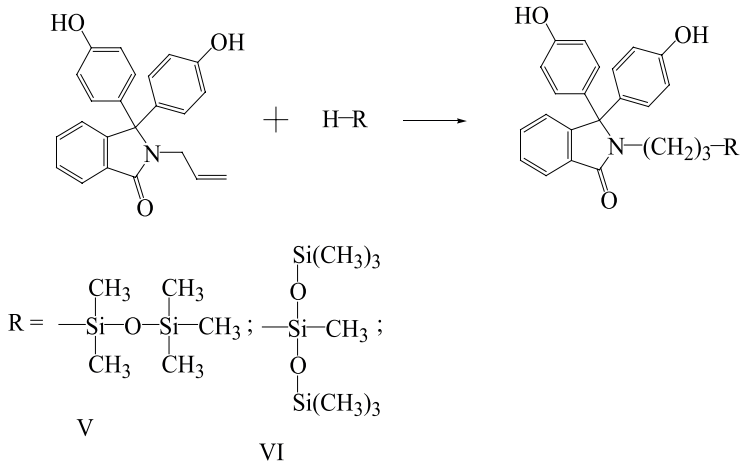


Scheme 1. Reaction of phenolphthalein with γ-aminopropylorganosiloxane.

[1] Raigorodskii I.M., Kirilin A.D. *Poliorgano-polisiloksanovye sopolimery* (*Polyorgano-Polysiloxanes Copolymers*). Moscow: MIREA RTU; 2018. 192 p.
[2] Salazkin S.N. Research in the field of phenolphthalein polyarylates and its derivatives. Cand. Sci. Thesis, Moscow, 1965. 146 p.



Scheme 2. Products of phenolphthalein interaction with γ-aminopropylorganosiloxane.



Scheme 3. Reaction excluding the rearrangement of the Si–O–Si bond and creating only bis-phenols with a grafted siloxane phthalimidine group.

dioxane, isopropyl alcohol, hexane, triethylamine (TEA), NaOH (*CHIMMED*, Russia). The ^{1}H NMR spectra of the products were recorded on a Bruker AT 360 MHz NMR spectrometer (*Bruker*, Germany). Deuterated chloroform, deuterated dimethyl sulfoxide (DMSO), and deuterated acetone (*Astrachem*, Russia) were used as solvents. Bis(chloroformate) diphenylolpropane (BCD) was prepared by adding dropwise liquid phosgene (*Korund*, Russia) in dichloromethane to a solution of diphenylolpropane (*VitaHim*, Russia) in dichloromethane with TEA. After recrystallization of BCD from hexane, bp = 92–94°C. Determination of the content of chloroformate groups in BCD (solution in dioxane) after the destruction of these groups with a 5% NaOH solution was carried out by potentiometric titration.

The preparation of compounds **V** and **VI** (Scheme 3), which were selected for further syntheses of PCS copolymers, is described below.

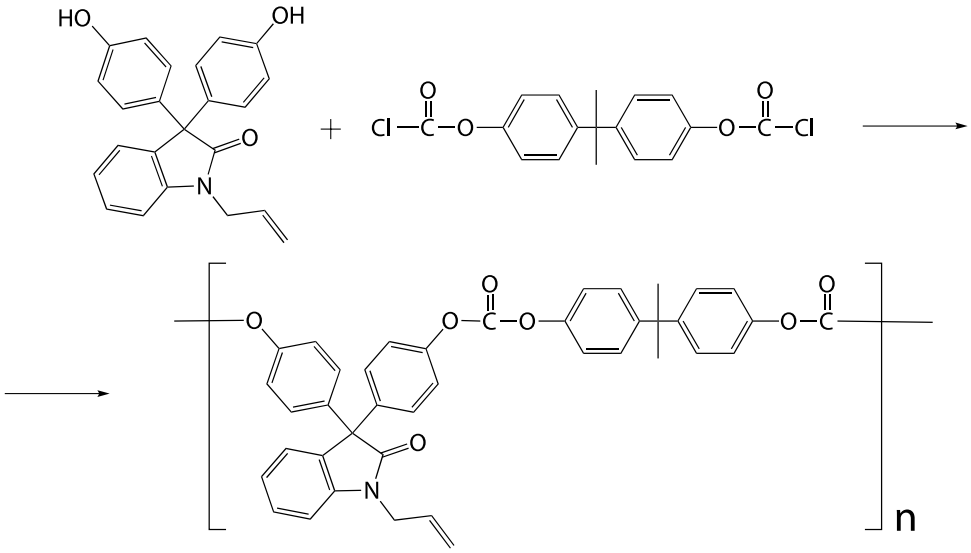
Synthesis of phenolphthalein N-[3-(1,1,3,3,3-pentamethyldisiloxane)propyl]phthalimidine of structural formula **V**. A reaction flask was loaded with 7.148 g (0.02 mol) phenolphthalein *N*-allylphthalimidine, 3.264 (0.022 mol) 1,1,3,3,3-pentamethyldisiloxane, 20 mL dioxane, and 1.3 mg of Karsted's catalyst (*Bayer*, Germany).

The reaction mass was stirred at 70°C for 4 h. The course of the reaction was monitored using the Chugaev–Tserevitinov method [10]. The solvent and excessive hydridesiloxane were distilled off in a rotary evaporator at a temperature of 90°C and a pressure of 2 mm Hg to yield 9.6 g of phenolorganosiloxane **V** (yield, 95 wt %). The reaction product was a white powdery substance soluble in acetone, DMSO, dioxane, and ethyl alcohol. The structure and composition of compound **V** were confirmed and characterized by NMR spectroscopy in deuterated acetone and elemental analysis. The proton signals in the NMR spectrum of compound **V** in deuterated acetone were as follows: H1: 7.03–7.06; H2: 6.79–6.82; H3: 7.70–7.72; H4: 7.48–7.52; H5: 7.40–7.44; H6: 7.36–7.38; H7: 3.33–3.38; H8: 0.92; H9: 0.26; H10: −0.12; H11: −0.01; H12: 8.45. The composition of compound **V** in wt % calculated/found was as follows: C 66.49/66.30; H 6.98/6.90; N 2.77/2.90; Si 11.11/11.30.

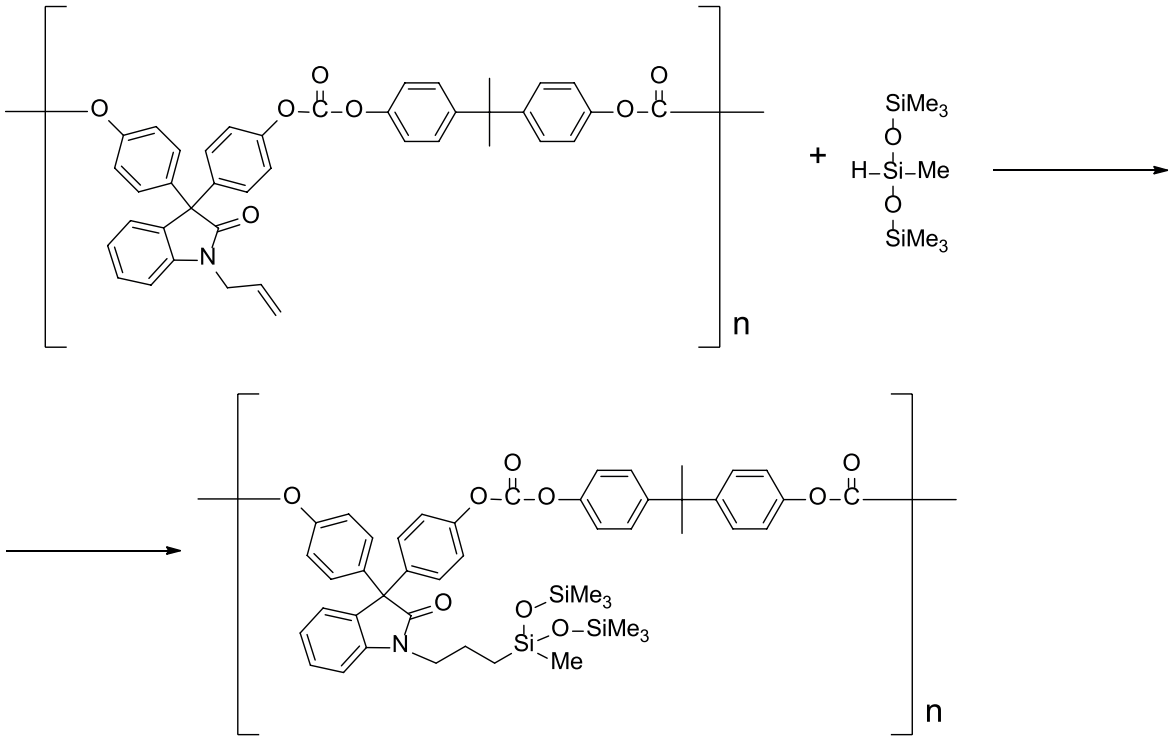
Synthesis of phenolphthalein N-[3-(1,1,1,3,5,5,5-heptamethyltrisiloxane)propyl]phthalimidine of structural formula **VI**. From 7.148 g (0.02 mol) phenolphthalein *N*-allylphthalimidine, 4.851 (0.022 mol) 1,1,1,3,5,5,5-heptamethyltrisiloxane and 12.45 g bisphenolsiloxane **VI** were obtained at a yield of 94 wt %. The reaction product was a white powdery substance soluble in acetone, DMSO, dioxane, ethanol, dichloromethane, and chloroform. The structure and composition of compound **VI** were confirmed and characterized by NMR spectroscopy in deuterated DMSO and using elemental analysis. The proton signals in the NMR spectrum of compound **VI** in deuterated DMSO were as follows: H1: 6.94–6.96; H2: 6.72–6.74; H3: 7.68–7.70; H4: 7.48–7.53; H5: 7.40–7.44; H6: 7.34–7.37; H7: 3.26–3.29; H8: 0.88; H9: 0.15; H10: −0.01; H11: −0.18; H12: 9.53. The composition of compound **VI** in wt % calculated/found was as follows: C 62.13/62.20; H 7.13/7.24; N 2.42/2.35; Si 14.53/14.45.

Synthesis of polycarbonate (PC-F) based on *N*-allyl-3,3-bis-(4'-hydroxyphenyl)phthalimidine and BCD was carried out by phase-transfer polycondensation (Scheme 4), where 7.14 g (0.02 mol) of *N*-allyl-3,3-bis-(4'-hydroxyphenyl)phthalimidine and 0.88 g (0.022 mol) NaOH were dissolved in 100 mL of water and 7.41 g (0.021 mol) BCD was dissolved in 100 mL dichloromethane. These solutions and 0.1 mL of triethylamine (as a catalyst) were loaded into a four-necked flask equipped with a reflux condenser, thermometer, and stirrer. The reaction was carried out at 5–10°C. The course of the reaction was monitored by the disappearance of chloroformate groups (analytical test for phosgene). Then, the reaction mixture was acidified to render it mildly acidic, washed with water, and the product was precipitated in 300 mL isopropyl alcohol. The polymer was dried at 120°C for 5 h. As a result, 12.3 g PC-F was obtained.

Synthesis of siloxanepolycarbonate (PC-SC-I) according to Scheme 5 was carried out by the polymer-analogous transformation of the PC-F polymer (Scheme 4). A four-necked flask equipped with a reflux condenser, a thermometer, and a stirrer was loaded with 7.6 g PC-F dissolved in 60 g dioxane and 0.3 mg of Karsted's platinum catalyst; 2.65 g 1,1,1,3,5,5,5-heptamethyltrisiloxane dissolved in 10 g dioxane was added in a dropwise manner. The reaction was carried out at 90°C. The course of the reaction was monitored by the Chugaev–Tserevitinov method. After completion of the reaction, the solvent and unreacted hydride were distilled off on a rotary evaporator. The polymer was



Scheme 4. Synthesis of polycarbonate (PC-F).



Scheme 5. Synthesis of siloxane polycarbonate (PC-SC-I).

dried at 120°C for 5 h. As a result, 9.9 g of PC-SC-I copolymer was obtained.

According to the ^{1}H NMR data, the ratio of the integral intensities of the proton signal of the phthalimidine ring in the region of 7.89 ppm to –Si(CH$_3$)$_3$ protons was 1 : 13.5, and the ratio to the protons of the 4.05–5.20 allyl fragment was 1 : 0.68. Thus, the hydrosilylation conversion was ~75%.

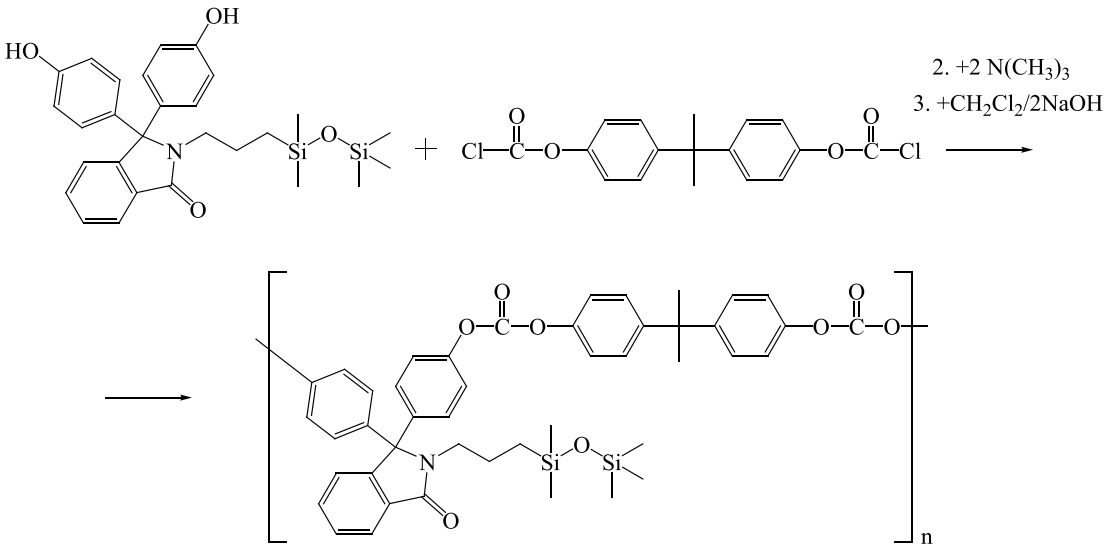
Synthesis of siloxane polycarbonate (PC-SC-II) according to Scheme 6 (option 2) was carried out from *N*-(3-(pentamethyldisiloxane)propyl)-3,3-bis-(4'-hydroxyphenyl)phthalimidine and BCD in a solution using triethylamine as an acceptor of hydrochloric acid. A four-necked flask was charged with 5.8 g (0.01 mol) *N*-(3-(pentamethyldisiloxane)propyl)-3,3-bis-(4'-hydroxyphenyl)phthalimidine, 50 mL dichloromethane, and 2.12 g (0.021 mol) trimethylamine. Additionally, 3.53 g (0.01 mol) BCD, dissolved in 50 mL of dichloromethane, was added dropwise to the mixture. The reaction was carried out at 10°C until the analytical reaction indicated the disappearance of the chloroformate groups. The reaction mixture was washed with a diluted solution of hydrochloric acid and then with water until neutral. The product was precipitated in 300 mL isopropyl alcohol and dried at 120°C for 5 h. As a result, 9.3 g of the copolymer was obtained.

Synthesis of siloxane polycarbonate (PC-SC-III) according to Scheme 6 (option 3) from *N*-(3-(pentamethyldisiloxane)propyl)-3,3-bis-(4'-hydroxyphenyl)phthalimidine and BCD was carried out by phase-transfer polycondensation. Here 5.8 g (0.01 mol) of *N*-(3-(pentamethyldisiloxane)propyl)-3,3-bis-(4'-hydroxyphenyl)phthalimidine was dissolved in a 1 g (0.025 mol) alkaline solution of NaOH per 100 mL of water. BCD (3.7 g, 0.0105 mol) was dissolved in 100 mL dichloromethane; 0.1 g triethylamine was used as a catalyst. The analytical reaction was carried out at 10°C until the disappearance of the chloroformate groups was indicated. The reaction mixture was washed with a diluted solution of hydrochloric acid and then with water until neutral. The product was precipitated in 300 mL isopropyl alcohol and dried at 120°C for 5 h. Subsequently, 9.5 g of the copolymer was obtained.

Figure 1 shows the NMR spectra of the PC-F and PC-SC-II polymers. Peaks at 1.67 ppm correspond to the CH$_3$ groups in propane; peaks at 4.1, 4.73, and 5.18 are attributed to the allyl chain; signals at 7.48 and 7.89 are attributed to protons of the phthalimidine ring; signals at 7.14–7.3 are attributed to –CH= of the phenolic fragments. The –0.16 peak is attributed to ≡Si–CH$_3$ and the 0.01 peak to –Si(CH$_3$)$_3$.

RESULTS AND DISCUSSION

The synthesized PCS copolymers were white powdery substances readily soluble in dichloromethane, chloroform, dioxane, tetrahydrofuran, and DMSO. The properties of PCS with lateral siloxane fragments are presented in Table 1.



Scheme 6. Synthesis of siloxane polycarbonate (PC-SC-II) (option 2) and siloxane polycarbonate (PC-SC-III) (option 3).

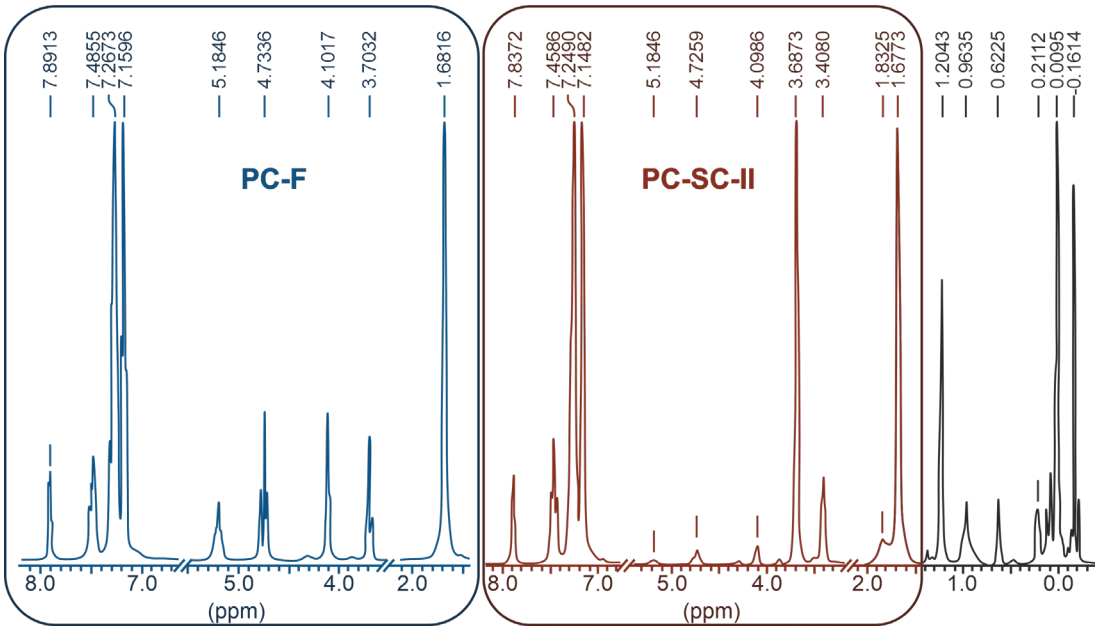


Fig. 1. ^{1}H NMR spectra of copolymers PC-F and PC-SC-II.

It follows from Table 1 that it is possible to obtain copolymers with maximum viscosity (molar mass) by interfacial polycondensation of product **V** with BCD (Scheme 6, option 3). Copolymers PCS I–III containing 20–23 wt % of dimethylsiloxane units had a glass-transition temperature (T_{glass}) 13°C lower compared with the PC-F copolymer without them. Concurrently, PCS copolymers in the form of films obtained from 1% solutions in dichloromethane, and dried in the air at 20–60°C for 6 h, have a high tensile strength above 50 MPa and an elastic modulus of up to 2000 Mpa. In addition, the presence of dimethylsiloxane suspensions in PCS copolymers increased the elasticity of the films 1.5-fold.

One possible field of application for newly synthesized PCS copolymers is membrane technology. While conducting this study, it was necessary to evaluate the diffusion properties of PCS, taking into account the fact that PCS copolymers have a high glass-transition temperature, thermal stability, and good mechanical properties. The data on the coefficients of gas permeability through PC-SC-I

Table 1. Physicochemical properties of PC-F and PCS

Polymer cipher	η_{rel}, at 20°C	SiO groups' content, wt %	T_{glass}, °C	T, °C	Mechanical properties of 40-μm films		
					E_{el}, MPa	σ, MPa	ε_{rel}, %
PC-F	0.9	–	175	335	2450	62.8	5.5
PC-SC-I	0.6	20	162	360	1920	58.6	9.0
PC-SC-II	0.4	23	160	355	–	–	–
PC-SC-III	1.3	23	163	358	2000	50	8.0

Note: η_{rel} – relative viscosity; T_{glass} – glass-transition temperature; E_{el} – elastic modulus; σ – tensile strength; ε_{rel} – elongation at room temperature, 20–25°C.

Table 2. Permeability and selectivity of PC-SC-I compared with PC and PCS-Ft-11

Sample cipher	Permeability coefficient, barrier						Selectivity of gas separation			
	N_2	O_2	CO_2	He	H_2	CH_4	O_2/N_2	CO_2/O_2	CO_2/N_2	H_2/CH_4
PC	0.29	1.48	6.0	–	–	–	5.1	4.1	20.7	–
PCS-Ft-11	0.55	2.66	15.53	18.3	16.6	0.87	4,.9	5.8	28.2	18.4
PC-SC-I	0.92	3.92	23.5	24.7	27.1	1.4	4.,3	6.0	25.5	19.4

Note: PCS-Ft-11 – fluorine-containing siloxane polycarbonate.

copolymers in the form of a film for N_2, O_2, CO_2, He, H_2, and CH_4 are presented in Table 2 to serve as a comparison with the permeability coefficients for industrial polycarbonates made of diphenylolpropane (PC) and fluorine-containing siloxane polycarbonate (PCS-Ft) [1]. The table shows that the presence of 20 wt % siloxane fragments in the PC-SC-I copolymer makes it possible to obtain a three-to-four-fold increase in permeability for most of the gases under study, without a significant drop in the selectivity of their separation. Additionally, it is possible to increase the permeability up to one-and-a-half times compared with a linear copolymer containing 30 wt % fluorosiloxane blocks.

CONCLUSIONS

New comb-shaped polycarbonate siloxanes were synthesized based on monomeric *N*-phthalimidine containing siloxy units using three polycondensation methods. It was shown that these products had high levels of thermal stability, strength properties, gas permeability, and selectivity, categories in which it outperformed linear copolymers of this class. Thus, the obtained results for the synthesis of new comb-like PCS, combined with high selectivity of gas separation, make it possible to use them as film membrane materials with an increased operating temperature range.

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Authors' contribution

D.O. Anashkin – consultation on the planning, methodology and implementation of the study;

I.M. Raigorodskii – analysis and selection of publications, writing the text of the article, formalization of the list of references;

A.D. Kirilin – consultation on chemistry of organosilicon compounds and individual stages of research;

P.A. Storozhenko – idea and design of the study, consulting on all stages of research.

The authors declare no conflicts of interest.

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