2604 *Russian Chemical Bulletin, International Edition, Vol. 53, No. 11, pp. 2604—2610, November, 2004*

New polysilalkylenes: synthesis and gas-separation properties

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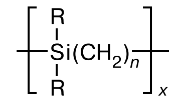
A series of polysiltrimethylenes with different substituents at the silicon atom, as well as new polydimethylsilmethylene, were synthesized by the ring-opening polymerization of the corresponding sila- and disilacyclobutanes. For the first time, the copolymerization of dimethylsila- and tetramethyldisilacyclobutanes was carried out with formation of permethylsilalkylene elastomers containing a controlled number of silmethylene and siltrimethylene units in the main chain. Permeability coefficients of *n*-alkanes C_1—C_4 were measured for the prepared silalkylene homopolymers and copolymers by mass spectrometric and barometric techniques. An analysis of the permeability, solubility, and diffusion coefficients indicated that the separation of hydrocarbons proceeded according to a solubility-controlled mechanism. Polysilalkylenes with various structures of radicals at the Si atom were applied onto the surface of porous hollow fibers. The study of gas-separation parameters of the obtained composite membranes showed that they dramatically depended on the type of substituents at the Si atom. The series of polypermethylsilalkylenes are promising as membrane materials for the separation of hydrocarbon gases.

Key words: silacyclobutanes, synthesis, polymerization, copolymerization, hydrocarbon gases, gas-separation properties, permeability, selectivity, polymer films, hollow fibers.

The use of polycarbosilanes as polymers appropriate for the creation of efficient gas-separation membranes takes origin from the 1960s. Numerous examples showed that the presence of a trimethylsilyl group in a monomeric unit always resulted in a substantial increase in the permeability coefficients of gases, being sometimes accompanied by an increase in the selectivity.[1—9] Trimethylgermyl groups exert a similar effect; however, germanium-containing polymers are studied in less detail.[10,11]

To separate hydrocarbon mixtures of composition C_1—C_4 according to molecular masses, one needs polymers in which separation is mainly determined by thermodynamic factors, *i.e.*, solubility coefficients. Membranes based on elastomers, for example, weakly cross-linked polydimethylsiloxane with the highest permeability coefficients[12] among rubbers, are used presently for this purpose. At the same time, Si—O bonds are known to possess a noticeable chemical activity,[13] which can limit the sphere of practical use of polysiloxane-based membrane materials.

For the separation of natural and casing-head gases, it seemed of interest to study heterochain polycarbosilanes, *viz.*, polysilmethylenes and polysiltrimethylenes containing Si—C bonds in the main chain



$$\left[\mathrm{Si(R)_2(CH_2)}_n\right]_x$$

n = 1, 3

It is known that many of these substances are chemo- and thermostable elastomers with low glass-transition temperatures (below −100 °C).[14] Since low glass-transition temperatures cause, as a rule, high permeability coefficients of rubbers,[15,16] polysilmethylenes and polysiltrimethylenes seem to be potential membrane materials for separation of gaseous hydrocarbons according to molecular masses.

The purpose of this work is to obtain new polycarbosilane polymers and systematically study their gas-separation properties.

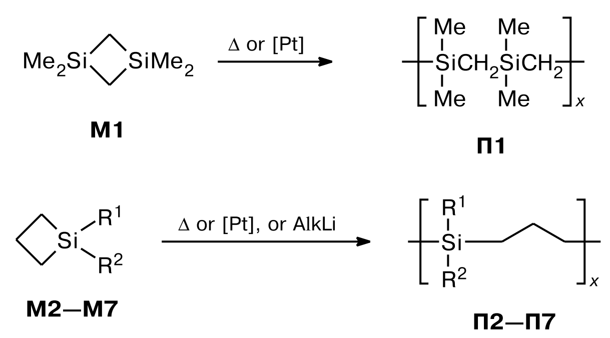
Polysilmethylenes (**P1**) and a series of polysiltrimethylenes (**P2—P7**) with different substituents at the silicon atom were synthesized by the thermal and catalytic polymerization of monomers **M1—M7** (Scheme 1).

Results and Discussion

Silacyclobutane derivatives with substituents at the Si atom are much more accessible than Si-substituted

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2497—2503, November, 2004.

Scheme 1



Compound	R^1	R^2
M2, P2	Me	Me
M3, P3	CH_2SiMe_2Ph	CH_2SiMe_2Ph
M4, P4	Me	CH_2SiMe_3
M5, P5	Me	$(CH_2)_3SiMe_3$
M6, P6	Me	*m*-Tolyl
M7, P7	α-Naphthyl	Cyclohexyl

disilacyclobutanes. Correspondingly, the related siltrimethylene polymers are also more accessible. Therefore, it is in a series of polysiltrimethylenes that the dependence of the properties of polymers on the structure of monomers was studied. As can be seen from Scheme 1, ring-opening polymerization performed by both thermal initiation and on the platinum catalyst developed by us afforded polysiltrimethylenes **P2**,[17] **P4**,[18] and **P5**[18] with different distances between the Me_3Si group and Si atom of the main chain and **P6**,[19] **P7**,[19,20] and **P3**, which, as well as the starting monomer 1,1-bis(phenyldimethylsilylmethyl)silacyclobutane, have been synthesized for the first time.

The permeability of hydrocarbon gases through the synthesized polymers was studied after the polymers were applied onto polysulfone or polyamide hollow fibers. Both individual gases and butane—methane mixtures were used. The permeability of the membranes $Q = P/l$ (P is the permeability coefficient, and l is the efficient thickness of the selective layer) depends on the thickness of the selective layer, pore size in the polymer support, degree of penetration of the membrane material into pores, and resistance in the porous sublayer. In the first approximation, for the series of membranes of the same type, the permeability can characterize, more or less correctly, the transport properties of a polymer in the selective sublayer.

We found that polydimethylsilmethylene (**P1**) possesses high selectivity at high gas permeability for the butane—methane pair (α ~40). The physicochemical properties of polysiltrimethylenes and polydimethylsilmethylene and their gas-separation characteristics with respect to methane and butane are presented in Table 1.

However, it turned out that even a high-molecular sample of **P1** (M up to $1 \cdot 10^6$) forms no stable films. The selectivity of polydimethylsiltrimethylene **P2** (α ~27) is somewhat lower than the expected value. At the same time, this crystalline polymer exhibited good film-forming properties. Due to the "magic" trimethylsilyl groups located at different distances from the Si atom of the main chain in polymers **P4** and **P5**, these polysiltrimethylenes retain high selectivities for the butane—methane pair (α 28.1 and 26.2, respectively) and remain elastomers with glass-transition temperatures of –51 and –46 °C, respectively. However, the permeability with respect to butane of the best of these polymers (**P4**) was almost 20-fold lower than that of **P1**. The selectivity with respect to hydrocarbons was more than twofold smaller for polysiltrimethylene with two rather bulky phenyldimethylsilylmethyl substituents (**P3**) (T_g = –36 °C) and the polymer with higher glass-transition temperature (**P6**) (T_g = –25 °C). Finally, the selectivity and permeability with respect to hydrocarbons decrease sharply for the glassy polymer with bulky cyclohexyl and α-naphthyl substituents (**P7**) (T_g = +47.5 °C). Thus, it is seen that the

Table 1. Some physicochemical properties, permeability of polymers, and factors of ideal separation for the composite hollow-fiber membranes (20 °C, pressure drop on the membrane is 1 atm)

Polymer	MW[a] (M_w/M_n)	T_g/°C (T_m[b]/°C)	Hollow fiber[c]	P/L m^{-2} h^{-1} atm^{-1}		α	
				O_2/N_2	C_4H_{10}/CH_4	O_2/N_2	C_4H_{10}/CH_4
P1	357000 (3.43)	–92	PS	79.6/39.8	3650/94.0	2.0	38.8
P1	1600000 (1.13)	–92	PA	55.1/20.5	2219/61.4	2.68	36.1
P2	1400000 (1.16)	–75 (+43)	PA	14.1/5.79	457/16.8	2.44	27.2
P3	1200000 (2.4)	–36	PA	71.9/29.9	1294/85.1	2.40	15.2
P4	1650000 (1.14)	–51	PA	5.04/2.0	194/6.91	2.52	28.1
P5	1420000 (1.2)	–46	PA	8.26/3.56	118/4.5	2.32	26.2
P6	760000 (1.44)	–25	PA	4.15/1.85	76.4/4.36	2.24	17.5
P7	270000 (2.53)	47.5	PA	4.37/1.38	7.4/6.1	3.17	1.2

[a] MW is the molecular weight.

[b] T_g is the glass-transition temperature, and T_m is the melting temperature.

[c] Polysulfone (PS) and polyamide (PA) hollow-fiber membranes.

Table 2. Permeability coefficients of polysilalkylenes at 25 °C: homopolymers and statistical copolymers

Polymer	P/Barrer*											
	O_2	N_2	CH_4	C_2H_6			C_3H_8			n-C_4H_{10}		
				$p \to 0$	$\Delta p \to 0$	$\Delta p = 0.4$	$p \to 0$	$\Delta p \to 0$	$\Delta p = 0.4$	$p \to 0$	$\Delta p \to 0$	$\Delta p = 0.4$
				atm								
P1[a]	99	40	130	—	345	364	—	434	837	—	1361	2807
P2[b]	9.5	3.0	8.4	10.6	—	26	13.5	—	37	14.3	—	240
CP3 (50/50)[a]	69	27	90	—	239	265	—	295	636	—	753	1748
CP3 (75/25)[b]	104	39	113	310	—	335	449	—	547	1163	—	2340
P1[23]	100	45	130	—	390	—	—	850	—	—	—	—

* 1 Barrer = 10^{-11} cm^3 (n.c.) cm cm^{-2} s^{-1} $Torr^{-1}$.

[a] Volumetric measurements at a pressure behind the membrane of 1 atm.

[b] Mass spectrometric measurements at a pressure behind the membrane of 10^{-3} Torr.

further are the properties of the polymers from elastomers and the closer to thermoplastics, the stronger the decrease in the selectivity with respect to hydrocarbon gases. At the same time, the selectivity with respect to oxygen and nitrogen of glassy polysiltrimethylene **P7** is somewhat higher.

Polydimethylsilmethylene (**P1**) is the most promising polymer for use as a material separating hydrocarbon gases (Table 2). It should be mentioned that the modern technology of gas separation on porous hollow-fiber membranes requires small amounts of a supported polymeric material, which holds promise for the practical use of comparatively expensive polysilmethylenes and polysiltrimethylenes.

Further studies of polydimethylsilmethylene (**P1**) were aimed at eliminating its main disadvantage: poor mechanical characteristics which prevent the formation of stable films. In principle, this problem can be solved by the direct controlled curing of **P1** (radiation-induced or chemical, in particular, peroxide-induced curing) or introduction into the polymer of a necessary amount of reactive functional groups (for example, unsaturated) by copolymerization of **M1** with co-monomers containing these groups. This would enable cross-linking following film formation. However, both these approaches were difficult to accomplish, the former because of the high chemical stability of **P1**, and the latter because of the labor-consuming preparation of the soluble functionalized silmethylene polymer.

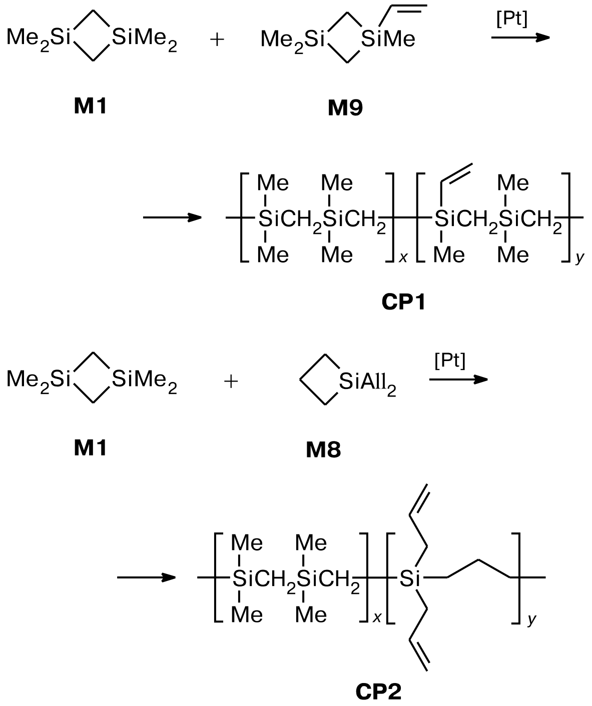
At the same time, certain success is achieved in the synthesis of soluble functionalized polysilmethylenes promising for controlled cross-linking after film formation. Copolymerization of monomer **M1** with alkenyl-containing silacyclobutanes both in the monomer bulk and in toluene at 155—165 °C or in the presence of Spier´s catalyst at 90—110 °C afforded the cross-linked copolymer in the course of the reaction. To decrease the copolymerization temperature and obtain high-molecular-mass soluble products with a narrow molecular-mass distribution, we developed a special catalyst. It was prepared from traditional Spier´s catalyst directly before experiment by heating it in an inert atmosphere and removal of the solvent and other volatiles by evacuation followed by sublimation (see Experimental). It can be assumed that propene formed upon dehydration of propan-2-ol forms a propene platinum complex due to π-bonding, which is much more active than Spier´s catalyst. Even at relatively low concentrations, the new catalyst polymerized and copolymerized silacyclobutanes under mild conditions (at temperatures ≤15 °C) to form homopolymers and soluble copolymers of monomer **M1** with co-monomers containing alkenyl groups (**M8** and **M9**) in yields higher than 95% (Scheme 2).

From the experiments on curing of these copolymers, it was proved that they are true copolymers. To prove that the copolymerization occurred indeed, a solution of each copolymer **CP1** and **CP2** and 1,1,3,3-tetramethyl-1,3-disiloxane in toluene (the ratio copolymer : cross-linking agent was ~10 : 1) and 0.1 equiv. of the catalyst (calculated with respect to platinum in the starting Spier´s catalyst) was refluxed for 2 h. Quantitative formation of a polymeric material totally insoluble in toluene (no traces of the polymer were found in solution) indicates its complete cross-linking and this fact, in turn, proves copolymerization. To confirm that this conclusion is correct, homopolymer **P1** was treated similarly and showed that no cross-linking occurred under these conditions and **P1** remained completely in solution.

The compositions of the copolymers were determined by ^{1}H NMR spectroscopy. However, attempts to perform the controlled curing of the copolymer with units containing two allyl groups (**CP2**) resulted in a sample with substantially lost permeability.

It was more fruitful to obtain a copolymer based on monomer **M1** and a monomer providing film-forming characteristics without radiation-induced or chemical cross-linking. The scope of appropriate co-monomers is

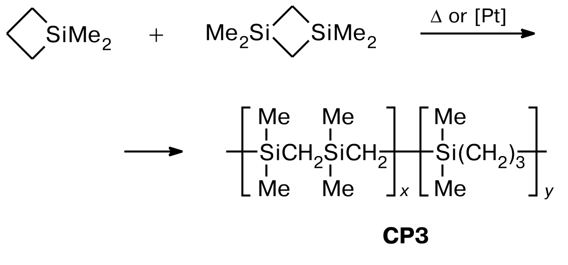
Scheme 2



highly limited, because monomer **M1** and other monomers of the 1,3-disilacyclobutane series copolymerize only with monomers of the same and silacyclobutane series.[20] Taking into account rather high permeability and selectivity with respect to hydrocarbons of homopolymer **P2** (see Table 1), we can hope to obtain a copolymer with high transport characteristics by copolymerization of **M1** and **M2**. Since **P2** possesses a high degree of crystallinity, one can expect a decrease in the fluidity of the copolymer for the statistical distribution of units. It seemed rather promising to combine the valuable properties of **P1**, first of all, high selectivity with respect to hydrocarbon gases, with the film-forming ability of **P2** possessing high selectivity.

We synthesized for the first time the corresponding copolymers[21] by copolymerization of methyl derivatives of mono- and disilacyclobutane (**M2** and **M1**) (Scheme 3).

Scheme 3



The process can be induced thermally or using the aforementioned catalyst. Catalytic copolymerization occurs to a larger extent and the composition of copolymers is closer to that of the initial monomer mixture than those in the case of thermal initiation (the yields of copolymers were at least 96—98%). The copolymerization of monomers **M1** and **M2** occurs successfully at 7—15 °C at a monomer-to-catalyst ratio of 10^4 : 1. Polymers remain colorless both after the end of polymerization and after precipitation with methanol and drying, while the use of Spier´s catalyst gives, in most cases, colored products. We found that copolymerization produces true copolymers (**CP3**) with the statistical unit distribution. This unambiguously followed from the presence of only one glass-transition threshold in the DSC curves for each copolymer (no melting peaks), while the specially prepared mixtures of **P1** and **P2** with the same compositions show distinct threshold corresponding to the glass-transition temperatures of both homopolymers. The compositions of copolymers **CP3** were determined by ^{1}H NMR spectroscopy from the ratio of integral intensities of signals for the protons of the "internal" methylene groups of the siltrimethylene units (δ ~1.33 in $CDCl_3$) and signals for the protons of the methyl groups at the silicon atom (δ –0.28—0.06). Some properties of prepared copolymers **CP3** of different compositions are presented in Table 3.

We have determined the parameters of hydrocarbon penetration through these new copolymers and found that they retained high selectivity and produced stable films. This especially concerns the 1 : 1 copolymer. In this case, the selectivity (α) with respect to the butane—methane pair reaches ~20 together with high permeability. It is most likely that such a happy situation where the copolymer acquires valuable properties of both homopolymers is explained by the fact that the homopolymers have similar chemical nature.

Statistical copolymers **CP3** obtained at the relatively high content of **P1** units have an amorphous structure and rather low glass-transition temperatures, which is promising with regard of the published data.[22—24] In this case, the permeability coefficients differ slightly from the coefficients for **P1** and, finally, demonstrate perfect film-forming properties. The permeability coefficients P of n-alkanes C_1—C_4 and air components are presented in Table 2.

Since the permeability coefficients of higher gaseous n-alkanes strongly depend on the pressure (see below),

Table 3. Properties of copolymers **M1** with **M2**

Copolymer	x/y	M_w	M_w/M_n	T_g/°C
CP3	80/20	740000	1.43	–83
	75/25	210000	1.87	–79.5
	50/50	88500	2.1	–76.5

the *P* values for different pressures at both sides of the polymer film are presented in Table 2. Measurements were carried out by mass spectrometry and volumetry for solid (homogeneous) films cast from a solution in chloroform. It is seen that in all polymers studied the permeability coefficients with respect to hydrocarbons increase with an increase in the size of a penetrant molecule. This behavior reflects a stronger influence of the solubility coefficients on the mass transfer rate rather than the influence of the diffusion coefficients as it takes place for mass transfer through glassy polymers. This can be illustrated by the data on the diffusion and solubility coefficients in these polymers presented in Tables 4 and 5. A comparison of the data in these tables shows that the main distinction between homopolymers **P1** and **P2** is determined by substantially lower diffusion coefficients of the latter. This can be related to both the higher glass-transition temperature of **P2** (lower segmental mobility at room temperature) and its partially crystalline structure.[25]

Butane is characterized by the especially strong dependences of the permeability coefficients of the studied hydrocarbons on pressure[26] (Figs. 1 and 2 illustrate this dependence for **P1** and one of the copolymers).

Since ideal factors of separation for the butane—methane pair were determined as $\alpha = P(C_4H_{10})/P(CH_4)$ and $P(C_4H_{10})$ depends strongly on the pressure, we can treat α values only as applied to certain pressures in front and behind the membrane. The ideal separation factors for this pair increase rapidly with the pressure increase (see Figs. 1 and 2). A comparison of the permeability coefficients of hydrocarbons penetrating through **P1** and copolymers **CP3** shows that these values are close indeed. In this case, good film-forming properties of the copolymer samples allow one to mold different composite membranes (planar and hollow-fiber) from these copolymers.

Thus, the polysilalkylenes studied with glass-transition temperatures below −45 °C demonstrate the high solubility-controlled selectivity in the separation of hydrocarbons C_1—C_4. Due to this, they can be considered as promising membrane materials to isolate higher hydrocarbons from their mixtures with methane.

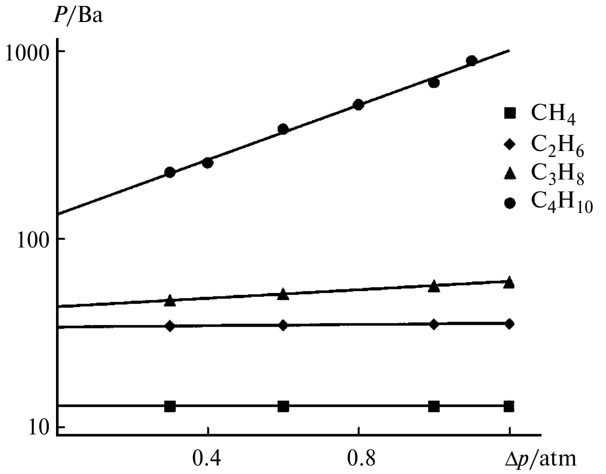


Fig. 1. Pressure plot of the permeability coefficients of polymer **P1** for *n*-alkanes (according to the data of volumetric measurements).

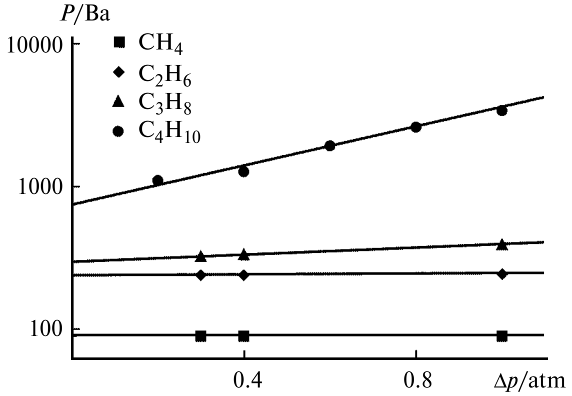


Fig. 2. Pressure plot of the permeability coefficients of copolymer **CP3** 50/50 for *n*-alkanes (according to the data of volumetric measurements).

Table 4. Solubility coefficients of polysilalkylenes at infinite dilution

Polymer	T/°C	S/cm^3 (n.c.) cm^{-3} atm^{-1}			
		CH_4	C_2H_6	C_3H_8	n-C_4H_{10}
P1	25	0.33	1.73	6.2	22.1
	10[25b]	0.37		9.8	
	35[25b]	0.32		4.6	
P2	25	0.45	2.5	9.5	36.4
CP3 (50/50)	25	0.51	2.3	7.1	22.7

Table 5. Diffusion coefficients in polysilalkylenes extrapolated to low pressures

Polymer	T/°C	$D \cdot 10^7$/cm^2 s^{-1}			
		CH_4	C_2H_6	C_3H_8	n-C_4H_{10}
P1	25	30	15	5.3	4.7
	35[23,25b]	33	—	14	—
P2	25	1.4	0.32	0.11	0.03
CP3 (50/50)	25	13.4	7.9	3.2	2.5

Experimental

^1H NMR spectra in $CDCl_3$ were recorded on a Bruker MSL-300 instrument (residual proton of solvent as the internal standard). Glass-transition temperatures of polymer samples were measured by the DSC method on a Mettler 4000 instrument. Molecular masses of polymers were determined by gel permeation chromatography using a Waters instrument for solutions in toluene using polystyrene standards for calibration.

Solvents used in the syntheses of monomers and polymers (THF, toluene, methanol) were prepared by standard methods. Solvents for solutions of polymer samples (*n*-hexane, cyclohexane) were distilled prior to use.

Monomers **M2**,[27] **M1**,[28] **M4** and **M5**,[18] **M6**,[29] **M7** [30] used for the syntheses of polymers and copolymers and monomers with unsaturated groups **M8** [31] and **M9** [32] were obtained by known procedures.

1,1-Bis(phenyldimethylsilylmethyl)silacyclobutane (M3). A solution of 1,1-dichlorosilacyclobutane (0.13 mol) in THF (330 mL) was added to a stirred solution of a Grignard reagent (prepared from 0.4 mol of phenyldimethylchloromethylsilane and 0.42 mol of Mg) in the same volume of THF at a rate that the temperature did not increase above 45 °C. After the end of addition, the mixture was refluxed for 4.5 h, cooled, and treated with water and aqueous ammonium chloride. After standard workup, the target monomer **M3** was isolated by distillation in 84% yield, b.p. 149—153 °C (~0.01 Torr), d_4^{20} 0.9649, n_D^{20} 1.5503. ^{1}H NMR, δ: 0.40 (s, 4 H, $SiCH_2Si$); 0.52 (s, 12 H, $SiCH_3$); 1.16 (t, 4 H, CCH_2Si); 2.18 (m, 2 H, CCH_2C); 7.50 (m, 6 H, *m*- and *p*-H_{arom}), 7.67 (m, 4 H, *o*-H_{arom}). Found (%): C, 68.32; H, 8.49; Si, 23.11. $C_{21}H_{32}Si_3$. Calculated (%): C, 68.40; H, 8.75; Si, 22.85.

Preparation of monomers for polymerization. Freshly distilled silacyclobutanes were stored over CaH_2 and condensed *in vacuo* into a reaction vessel. After rectification, disilacyclobutane **M1** was stored over metallic sodium and condensed into tubes for polymerization. Disilacyclobutane **M9** was first stored over CaH_2 and then over Na.

Thermally initiated polymerization[32] and polymerization on Spier´s catalyst[33,34] were carried out by known methods.

Preparation of the propene platinum complex and polymerization. Spier´s catalyst was placed in a tube heated *in vacuo* and filled with dry argon. The tube was heated for 20—30 min at ~140—150 °C and evacuated to remove the solvent and volatiles. Then the catalyst was sublimed onto the tube walls, a monomer or a mixture of co-monomers (with or without solvent) was introduced into the tube after cooling, and the tube was sealed and placed into a thermostat. When the increase in the viscosity of the reaction mixture ceased, the temperature was increased to room temperature or higher (to 100 °C). After cooling, toluene or benzene was added, and polymers were isolated by precipitation with methanol. The yields of polymers and copolymers were usually higher than 95 % and can reach ~100%.

The catalytic copolymerization of **M1** with monomers **M8** and **M9** was carried out similarly at ~15 °C and at the ratio of the sum of co-monomers to catalyst equal to 10^4 : 1 (Table 6).

Measurements of gas permeability characteristics for planar films. The permeability coefficients *P* of the studied polysilalkylenes were measured by mass spectrometry and volumetry. Experiments were carried out with individual gases at 25 °C. Solid (homogeneous) polymer films with the thickness within 50—100 μm were cast from chloroform solutions. The mass spectrometric procedure for measuring permeability has been described in detail.[35] Diffusion coefficients *D* were measured by the delay time using the classical Danes—Barrer method. The solubility coefficients *S* were estimated by the formula $S = P/D$. In mass spectrometric measurements, the pressure in front of the membrane ranged within 0—500 Torr, and the pressure behind the membrane was 1—2 atm. Volumetric measurements were carried out at a pressure behind the membrane of 1 atm and pressures in front of the membrane within 1—2 atm. The penetrant flow through the membrane was measured by a foam flowmeter.

Table 6. Some properties of copolymers **M1** with monomers **M8** and **M9** containing alkenyl groups

Copolymer	*x*/*y*	M_w	M_w/M_n	T_g/°C
CP1	99.9/0.1	106000	1.74	−92
CP2	96.2/3.8—93.4/6.6	620000	1.9	−74

Measurements of gas permeability characteristics for polymers coated onto hollow fibers. Hollow fibers of polysulfone or polyamide as tubes with porous walls were used (external diameter 1 mm, internal diameter 0.55 mm, direction of porosity increases from the inner to outer surface). Polysulfone or polyamide hollow fibers were coated with polymeric materials from solutions in *n*-hexane or cyclohexane with approximately equal concentrations (0.3—0.5 wt.%). According to the commonly accepted practice, a solution of polymer was supported from the side of finer pores (in this case, from the internal side) by using the vacuum method at 10^{-2} Torr. Subsequent drying was carried out at the same pressure. The thickness of coated polymeric films was 0.8—1.0 μm. The characteristics of gas flows passed through membranes were measured by the volumetric method. The uniformity of polymeric coatings (number of defects) was determined by measuring the fiber permeability at different gas pressure drops on the membrane. The linear dependence of the permeability of an individual gas through the fiber on the partial pressure drop of the gas at the fiber indicated than the gas-separation layer had no defects.

The authors thank M. P. Filatova for measuring ^{1}H NMR spectra.

This work was financially supported by the NATO Science for Peace Program (Grant 972638).

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Received June 1, 2004;
in revised form September 6, 2004