Synthesis and Permeability Properties of Crosslinkable Elastomeric Poly(vinyl allyl dimethylsilane)s

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ABSTRACT: This article presents the results of a systematic synthesis study of elastomeric crosslinkable polysilicon olefins, the related thermal crosslinking kinetics, and the main permeability parameters recorded for inorganic gases (He, N_2, O_2, and CO_2) and C_1–C_7 hydrocarbons. Poly(vinyl allyl dimethylsilane) (PVADMS; glass-transition temperature < 273°K) was obtained by the anionic polymerization of bifunctional vinyl allyl dimethylsilane monomer. The polymers were amorphous, high molecular compounds with mixed carbo-heterochain structures containing double bonds capable of intermolecular crosslinking under a thermal treatment. Thus, thermally crosslinked polymers exhibited a high resistance toward exposure to organic vapors, unlike noncrosslinked PVADMS. IR spectroscopy was used to investigate the polymer structural changes induced by the thermal treatment. An original technique based on a differential method was used to measure gas permeability during thermal crosslinking. PVADMS possessed higher permeability for C_1–C_7 hydrocarbons than for inorganic gases (excluding CO_2), even after crosslinking. Permeability coefficients ranging from 140 to 1780 Barrer for He and CH_4 were found before crosslinking; the thermal crosslinking induced a nonlinear permeability decrease that could be correlated with the disappearance of the double bonds in the polymer structures, that is, *cis*-CH=CH—, *trans*-CH=CH—, and CH_2=CH— in the side-chain position. According to the found properties, PVADMS could be used as a prospective material for the preparation of highly permeable selective membranes suitable for lower hydrocarbon and volatile organic compound recovery from various chemical and petrochemical process streams. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 927–935, 2005

Key words: anionic polymerization; crosslinking; gas permeation; infrared spectroscopy; polysilanes

INTRODUCTION

Membrane technology for the separation and purification of gaseous mixtures is a quickly growing research area for applications in various fields, including the chemical, petrochemical, pharmaceutical, and food industries and biotechnology. Membranes based on glassylike polymers are mainly used in air separation, CO_2 and water vapor removal from natural gas, and hydrogen recovery from industrial streams.[1] Moreover, improved membrane technology for lower hydrocarbon and volatile organic compound recovery from gaseous streams is expected to contribute to the development of clean and environmentally friendly technologies and to the recovery of energy carriers from renewable, natural, and industrial sources. In targeted gas mixtures, the organic compounds are present as a rule as minor components. In this case, membranes must have preferable permeability for organic compounds rather than permanent (inorganic) gases;[2] they must have high resistance toward the attack of the organic components of the studied mixtures as well.[3] Rubberlike polymers are suitable for this kind of application, but the choice of such polymers is very limited,[4] and few publications have reported the preparation of stable siloxane elastomers.[5,6] Commercially available membranes from rubberlike polymers [e.g., polydimethylsiloxane (PDMS)] for the separation of organic vapors have limited separation selectivity and possess poor film-creation ability, rather low mechanical properties, and limited stability against the attack of concentrated vapor mixtures.[7] Membranes based on glassylike polymers with low free volumes, such as widely used cellulose acetate[8,9] and polysulfone,[10] may not be used for the separation of hydrocarbons because they are more selective toward smaller molecules, that is, inert gases.[11] De-
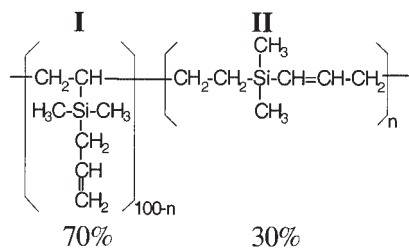
Figure 1 PVADMS structures are composed of two fragments. Fragment I with a vinyl side group can be used for further crosslinking reactions. Fragment II is responsible for the rubbery characteristics of the polymer.

sired membranes can be obtained from elastomeric polymer materials containing functional groups capable of intermolecular crosslinking.

This article presents the results of a systematic study aimed at the synthesis of vapor-solvent-resistant poly-(vinyl allyl dimethylsilane) (PVADMS), which is a rubbery polymer. The thermal crosslinking kinetics of PVADMS were investigated, along with the main permeability parameters of inorganic gases and C_1–C_7 hydrocarbons in this class of highly permeable elastomers.

EXPERIMENTAL

Materials

The structural formula of vinyl allyl dimethylsilane (VADMS) based polymers is shown in Figure 1. PVADMS was obtained through the anionic polymerization of the bifunctional VADMS monomer in bulk under various initial initiator concentrations, which allowed us to prepare polymers with different average
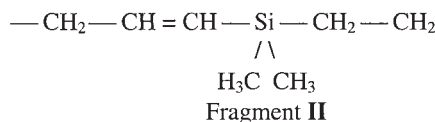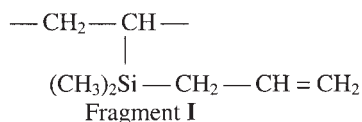
molecular weights. Because of the different reactivities of the double bonds of the monomer, the obtained polymer contained functional double bonds in the macrochain and in the organosilicon side chain; therefore, the polymer architecture enabled the flexibility of the polymeric chain and the latent formation of chemically crosslinked polymeric structures.[12,13]

The VADMS monomer was synthesized through the reaction of vinyl allyl dimethylsilyl chloride (Aldrich Chemical, Milwaukee, WI) and phenyl magnesium bromide according to the organomagnesium synthesis method, as described by Petrov et al.[14] The polymerization conditions and polymers molecular weights are given in Table I. The molecular weights of the polymers were determined with osmometry and gel permeation chromatography (Waters instrument with an R-401 differential refractometer, Milford, MA). The glass-transition temperatures (T_g's) were determined with differential scanning calorimetry (TA-3000, Mettler, Columbus, OH).

The elemental compositions of the polymers corresponded to the elemental composition of the monomer, and this means that polymerization took place through double bonds as expected (found: 22.30% Si, 66.52% C, and 11.18% H; calculated: 22.24% Si, 65.58% C, and 11.18% H).

Polymerization through vinyl group was also confirmed by the absence in IR spectra of absorption bands corresponding to vinyl groups directly linked to silicon and by the absence in ^{1}H- and ^{13}C-NMR spectra of the respective chemical shifts.

The PVADMS structure could be characterized by the presence of two distinct substructures named fragment I and fragment II:

$$--CH_2--CH--$$
$$|$$
$$(CH_3)_2Si--CH_2--CH=CH_2$$
Fragment **I**

$$--CH_2--CH=CH--Si--CH_2--CH_2$$
$$/\backslash$$
$$H_3C\ \ CH_3$$
Fragment **II**

The presence of fragment I was strongly confirmed by the appearance in IR spectra of bands characteristic of allylic structures connected at the silicon atom and by the respective chemical shifts in ^{1}H- and ^{13}C-NMR spectra.

^{1}H-NMR (δ, ppm): 0.17 m (SiMe$_2$), 1.50 d (SiCH$_2$—), 4.6–4.95 m (CH$_2$=), 4.5–6.2 m (—CH=). ^{13}C-NMR (δ, ppm): 23.4 (SiCH$_2$—), 113.2 (CH$_2$=), 135.0 (—CH=).

TABLE I
Conditions of the Bulk Polymerization of VADMS and the Characteristics of PVADMS

PVADMS	Monomer/initiator	[VADMS] (mol/L)	[sec-C$_4$H$_9$Li] (10^{-3} mmol/L)	Yield (wt %)	[η] in toluene at 25°C (dL/g)	M_w (× 10^3)	M_n (× 10^3)	M_w/M_n	T_g
1	100	5.75	57.2	65.5	0.08	17.7	10.3	1.72	−45.8
2	5000	5.90	1.18	50.6	0.62	316	64.5	4.90	−30.3

Polymerization temperature = 22°C. M_w = weight-average molecular weight; M_n = number-average molecular weight; [η] = intrinsic viscocity.
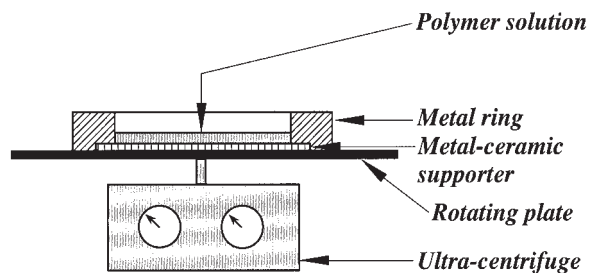
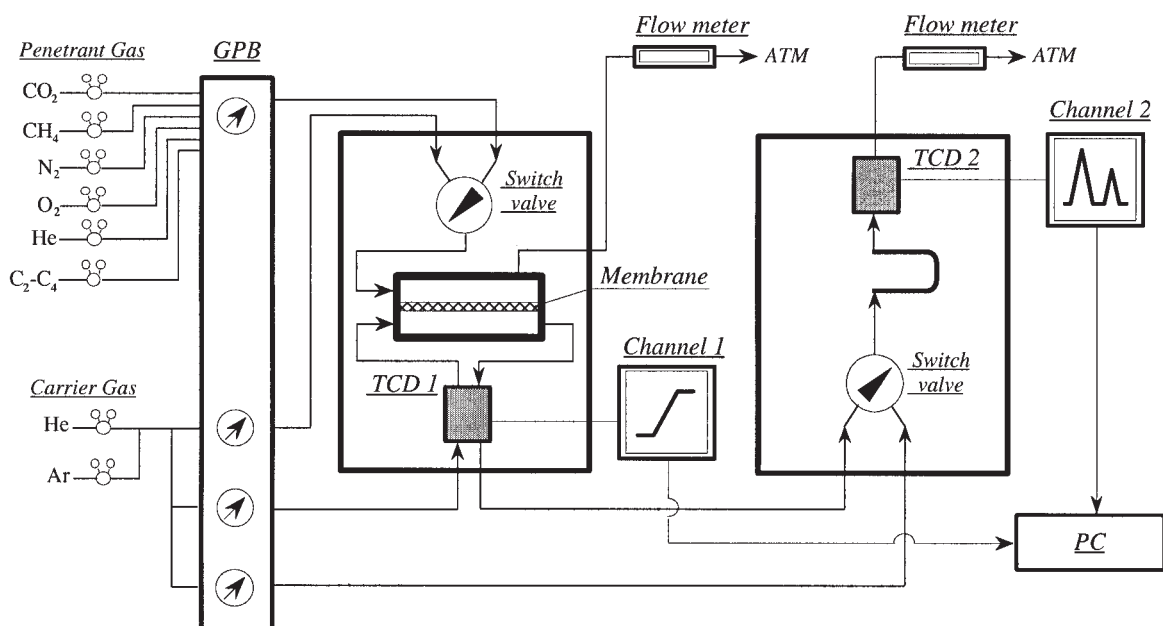**Figure 2** Rotating device used for the preparation of non-crosslinked membrane films from polymer solutions.

The presence of fragment II was also assessed with NMR and IR spectra.

^{1}H-NMR (δ, ppm): 0.25 m (SiMe$_2$), 1.9–2.4 m (—CH$_2$—), 5.4–6.2 m (—CH=CH). ^{13}C-NMR (δ, ppm): 14.2 (CH$_2$Si), 36.9 (*CH$_2$—CH=), 148.3 (=CH—CH$_2$), 128.9 (SiCH=).

In IR spectra, the band related to the substituted —CH=CH—Si group had a wave number of 1620 cm^{-1}.

The quantitative determination of substructures I and II was conducted via ^{1}H-NMR with the integral signal intensity of the protons in the allylic group (CH$_2$=; A_1) and the protons in the propenylic group (—CH=CH—; A_2):

$$\frac{A_2 - A_1/2}{(A_2 - A_1/2) + A_1} \times 100 \qquad (1)$$

This took into account the overlapping of the allylic CH= of fragments I and II.

Thus, the obtained polymers were determined by X-ray and NMR analysis[13] to be amorphous, high molecular compounds with a mixed carbo-heterochain structure containing double bonds capable of intermolecular crosslinking under a thermal treatment.

Preparation of the membrane films

Membranes for gas permeability characterization were prepared by two methods so that crosslinked or noncrosslinked structures were obtained. In the first standard method, the films were cast from a polymer solution in toluene onto a cellophane support. The concentration of the polymer in the solution was carefully controlled to obtain film thicknesses of approximately 100 μm. After solvent evaporation, the films were thermally treated under the desired conditions, and the obtained crosslinked polymer film was removed from the cellophane support.

In the second method, the polymer solution was poured onto a rotating metal–ceramic porous support (Trumen, Moscow, Russia) with a well-defined average pore size of 0.1 μm surrounded by a metal ring (Fig. 2); the solvent was vaporized instantly and left a noncrosslinked thin membrane film. The measurement of the gas permeability was carried out directly for membranes formed on the porous metal–ceramic support before any thermal treatment was applied, that is, as noncrosslinked structures, and during the crosslinking process.

Figure 3 Schematic diagram of the installation used to measure the gas-transfer parameters of membranes [GPB = gas preparation block; GC = gas chromatograph; channel 1 = signal to a personal computer (PC) for diffusion coefficient determination; channel 2 = signal to a PC for permeability determination].
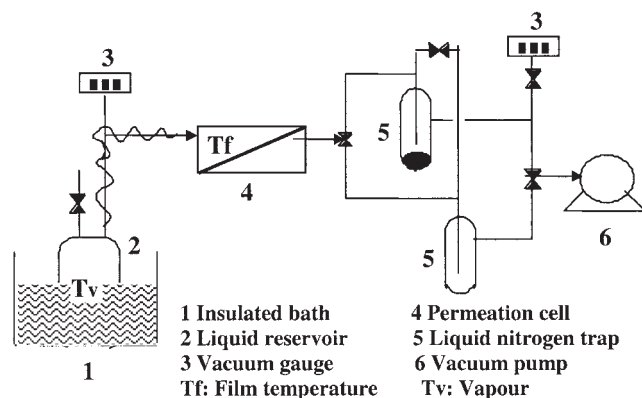
1 Insulated bath   4 Permeation cell
2 Liquid reservoir   5 Liquid nitrogen trap
3 Vacuum gauge   6 Vacuum pump
Tf: Film temperature   Tv: Vapour

Figure 4 Schematic diagram of the installation used to measure vapor-transfer parameters from pure components. The vapor is generated above the liquid reservoir, which is maintained at the vapor temperature (T_v), and comes into contact with the membrane film at the film temperature (T_f). Permeation through the film occurs under a pressure-gradient concentration driven by the vacuum pump, and the vapor is trapped continuously under steady-state conditions.

Characterization of the polymer structural modifications during crosslinking

IR spectroscopy was used to investigate the changes in the polymer structure under the applied thermal treatments. The IR measurements, ranging from 400 to 4000 cm^{-1} (Specord-M82, Carl-Zeiss Jena, Germany), were carried out as follows. A PVADMS solution in benzene was poured onto pressed KBr pellets and was kept in air until the complete evaporation of benzene; this led to thin films of about 15 μm. The initial measurements were registered for the noncrosslinked polymer film samples at room temperature and at 120, 140, and 150°C just before the beginning of the thermal treatment. Then, the polymer samples were thermally treated in air at 120, 140, and 150°C for 15, 30, 90, 160, 180, and 300 min, and IR spectroscopy was successively recorded for each set of conditions.

Method and apparatus for the measurement of the permeability parameters

Gas and vapor permeability parameters were measured with the differential method (DM) of permeability with original equipment developed at the A. V. Topchiev Institute of Petrochemical Synthesis and with the integral method (IM) developed at ENSIC, LSGC. For the DM measurements, there was a partial pressure drop of 1 bar across the membrane, and the temperature was 35°C. The installation was equipped with two thermal conductivity detectors (TCDs) for the separate determinations of the transient and steady-state fluxes (Fig. 3). A detailed description of the setup was previously reported.[15,16]

For the IM measurements, there was an absolute pressure drop of 1 bar across the membrane, the vapor activity varied up to 0.6, and the temperature was 35°C (Fig. 4). The vapor permeability measurements were recorded in the steady state with constant vapor activity of heptane or toluene; more details can be found elsewhere.[17]

RESULTS AND DISCUSSION

T_g's and mechanical properties

PVADMS materials were elastomers with low T_g's. By analogy with polymers synthesized from monofunctional vinyl silanes, PVADMS might have been expected to be a polymer with a high T_g, but that was not the case.[18] However, because of isomerization polymerization, the obtained PVADMS contained a silicon atom in the main chain and had, therefore, a lower T_g than expected (Table II). The presence of heterochain fragment II provided two important properties for the polymer structure that were very useful from a practical point of view: the increased flexibility of the polymer chains (low T_g) and the ability of crosslinking with a thermal treatment.

### Changes in the polymer structure with the thermal treatment (IR spectroscopy)

As shown in Figure 5, the characteristic bands for the saturated —CH$_2$— group at 2960, 2912, and 2856 cm^{-1} (ν CH$_2$, stretching vibrations) and at 1448 cm^{-1} (δ CH$_2$, deformation vibration) and for the —Si(CH$_3$)$_2$— bands at 1248 cm^{-1} (δ CH$_3$) and at 832 cm^{-1} (ν Si—C) were present in the IR spectrum for the noncrosslinked polymer. Bands indicating the presence of

TABLE II
Characteristics of the Crosslinked Polymers Based on VADMS

PVADMS sample number	M_w ($\times 10^3$)	Thermal-treatment temperature (°C)[a]	T_g (°C)	Tensile strength (5 mm/min, 25°C; kg/cm^2)	Elongation at break (5 mm/min, 25°C, %)
1	17.6	120	−24	60	43
2	316	120	−26	70	48
2	316	160	−23	—	—

[a] For 5 h.
M_w = weight-average molecular weight.
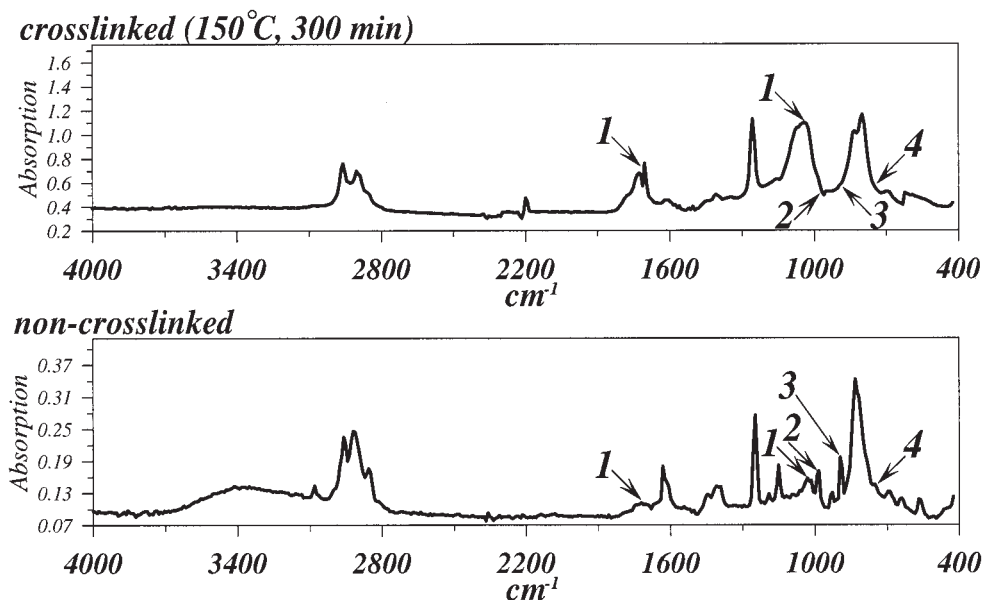
Figure 5 Changes in the absorption bands of IR spectra of PVADMS before and after a thermal treatment at 150°C (room atmosphere): (1) oxygen-containing groups (1710 and 1030 cm^{-1}), (2) bond;CH=CH— trans (970 cm^{-1}), (3) CH$_2$=CH—CH$_2$— allyl (890 cm^{-1}), and (4) —CH=CH— cis (750 cm^{-1}).

unsaturated groups could also be observed in the spectrum at 3080, 3066, and 3034 cm^{-1} (ν C=CH), at 1632 and 1618 cm^{-1} (ν C=C), and at 980, 928, 890, and 750 cm^{-1} (δ =CH and δ =CH$_2$), and the characteristic bands at 3080, 1632, 980, and 750 cm^{-1} indicated the presence of trans (970 cm^{-1}) and cis (750 cm^{-1}) configurations in the double bonds (—CH=CH—). On the other hand, the bands at 3066, 3034, 1618, 928, and 890 cm^{-1} characterized side-chain allyl groups. Therefore, the characterization of these bands proved the presence of fragments of type I and II in the studied polymers (see Fig. 1). The quantity of each type of fragment was determined through an analysis of the extinction coefficients of the absorption bands of cis, trans, allyl, and Si—C (696 cm^{-1}) bonds. The fragment ratio was 70:30 I/II for all the obtained polymers. Moreover, the ratio of cis and trans configurations was 20:80, and the data were in good agreement with the ^{1}H-NMR analysis results.[16] For the polymer heated at 150°C for 300 min, the total disappearance of the characteristic bands of the unsaturated groups was observed, whereas intensive bands appeared at 1730–1700 and 1000–1100 cm^{-1}, which were characteristic of the stretching vibrations of C=O and C—O bonds, respectively. On the basis of these results, we suggest the following assumption: during the thermal treatment under the room atmosphere, the crosslinking process of the polymer included the formation of peroxides because of the action oxygen, which decomposed into free radicals, inducing in turn the polymerization of unsaturated chains and hence the formation of the crosslinked polymers.

With the thermal treatment of the polymer, the —CH=CH— groups in the cis configuration (frag-

ment II) were much more reactive than the other unsaturated groups of the polymer, that is, the trans-CH=CH— groups (fragment II) and the allyl groups (fragment I), as shown on Figure 6. At the same time, absorption bands that could be related to various oxygen-connected structures were observed (Fig. 7). Moreover, through a comparison of the changes in the content of oxygen-containing groups and that of the double bonds, we found that the content of oxygen-containing groups in the polymer did not substantially change anymore when the cis-CH=CH— bonds were completely consumed, even though a slow reduction in the contents of the trans and allyl groups continued.

Therefore, these observations made during the thermal treatment supported our initial assumption: the
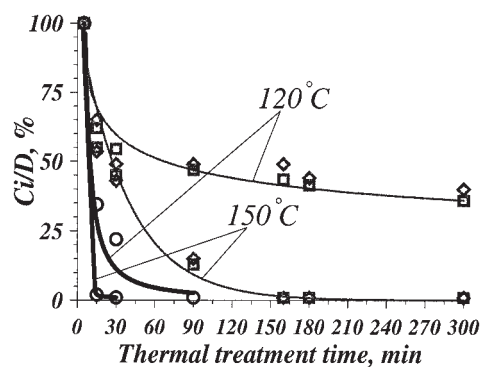
Figure 6 Kinetic curves of the disappearance of double bonds during the thermal treatment of PVADMS at different temperatures: (○) cis (750 cm^{-1}), (◇) trans (970 cm^{-1}), and (□) allyl (890 cm^{-1}).
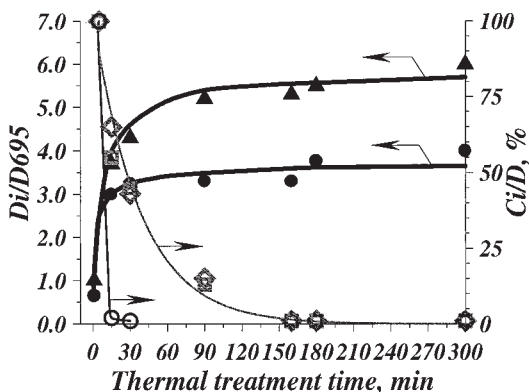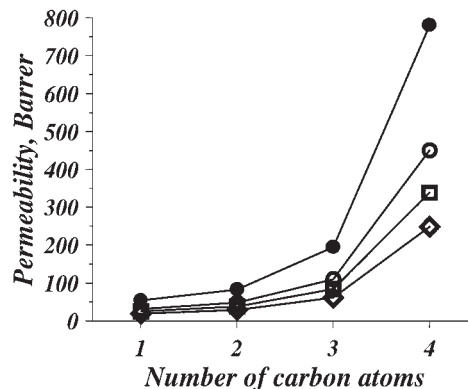
Figure 7 Kinetic curves of the disappearance of double bonds and the appearance of oxygen-containing groups during the thermal treatment (150°C) of PVADMS: (○) cis (750 cm^{-1}), (◇) trans (970 cm^{-1}), (□) allyl (890 cm^{-1}), (●) oxygen-containing bond (1710 cm^{-1}), and (▲) oxygen-containing bond (1030 cm^{-1}).

Figure 8 Dependence of the permeability of *n*-alkanes in PVADMS on the number of carbon atoms in an *n*-alkane molecule at 120°C: (●) 0, (○) 15, (□) 30, and (◇) 60 min.

crosslinking process of the polymer was caused by the fast oxidation of fragment II in the cis form by oxygen, followed by the formation of unstable peroxide connections and by the disintegration products of those unstable peroxide bonds. The resulting carbon radicals promoted not only the formation of interchain oxygen-containing connections but also the initiation of the crosslinking process.

Effect of crosslinking on the selective gas-transfer parameters

The regularity of permeability parameters of inorganic gases and lower hydrocarbons in polymers can be divided into two main types: in glassy polymers, inorganic gases typically have higher permeability than hydrocarbons, whereas the opposite tendency can be observed in highly rubbery polymers. In this study, the selective permeability of PVADMS (elastomer) with the variation of its crosslinking extent was investigated.

First, the effect of the initial molecular weight of the noncrosslinked polymers on the gas permeability parameters of the thermally crosslinked membranes was

studied. The experimental results showed that the molecular weight of the initial noncrosslinked polymers did not have an appreciable effect on the gas permeability parameters of crosslinked PVADMS (see Table III, membranes 1 and 2), and this meant that crosslinking occurring during the thermal treatment took place at the level of the monomer chains. Therefore, polymers of different molecular weights might be used in the preparation of composite membranes with respect to the porosity parameters of a given support; to prepare a composite PVADMS membrane on a metal–ceramic support, a polymer of a higher molecular weight was used (Table III, membrane 3).

The permeability properties of PVADMS were determined before any thermal treatment: a noncrosslinked PVADMS structure, coated onto a support, showed the typical permeability properties of a rubber (Table III, membrane 3). The permeability of the hydrocarbons exceeded the permeability of the inorganic gases, and the permeability in a series of C_1–C_4 hydrocarbons increased with the number of carbon atoms in the alkane series (Fig. 8).

Upon the thermal treatment, that is, with an increase in the crosslinking extent, the modification of the polymer structure could be clearly related to the evolution of the polymer gas permeability properties

TABLE III
Gas Permeability of Noncrosslinked and Crosslinked PVADMS Samples of Different Molecular Weights

PVADMS membrane	M_w ($\times 10^3$)[a]	Support	Heat-treatment temperature (°C)	He	N_2	O_2	CO_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}
1	316	—	120	40.9	1.9	7.9	53.0	4.1	10.1	11.2	41.3
2	17.7	—	120	52.1	2.4	9.1	67.6	5.2	—	—	—
3	316	Metal–ceramic	untreated	142.1	19.3	59.1	364	54.6	83.7	195.1	780.8
3*	316	Metal–ceramic	120	46.4	1.9	7.7	59.5	6.2	8.1	10.2	39.7

M_w = weight-average molecular weight.
[a] Initial noncrosslinked polymers.

TABLE IV
Effect of the Thermal-Treatment Time (at 120°C) of PVADMS on the Gas Permeability of Permanent Gases (Barrer)

Heat-treatment time (min)	He	N_2	O_2	CO_2	CH_4	Permeability of CO_2/ Permeability of CH_4
0	142.1	19.3	59.1	364.0	54.6	6.7
15	96.7	10.9	34.6	220.0	32.1	6.9
30	85.0	8.9	28.4	181.0	25.6	7.1
60	73.4	6.6	22.1	146.3	19.4	7.5
90	—	5.2	18.5	129.6	16.0	7.8
160	—	3.1	13.0	92.5	10.2	9.1
300	46.3	1.9	7.7	59.5	6.2	9.6

TABLE V
Effect of the Thermal-Treatment Time (at 120°C) of PVADMS on the Permeability of Hydrocarbons (Barrer)

Heat-treatment time (min)	Permeability								
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_7H_{16}[a]	C_7H_8[a]	C_4H_{10}/CH_4	C_7H_{16}/PCH_4	C_7H_8/CH_4
0	54.6	83.7	195.1	780.8			14.3		
15	32.1	48.7	110.7	451.2	1700	13500	14.1	52	420
30	25.6	38.6	84.9	338.9			13.2		
60	19.4	29.4	62.4	248.8			12.8		
300	6.2	8.1	10.2	39.7	300	1520	6.4	48	245

[a] Measured at a vapor activity of 0.6.

(Tables IV and V): the permeability was reduced for all gases and vapors tested, including heptane and toluene. However, the highest value was noted for toluene vapors.

Moreover, the difference in the experimental results for the gas permeability parameters of the crosslinked structures prepared as freestanding films and as composite membranes (i.e., membrane 3* on a metal–ceramic support) was not appreciable (Table III). This certified a good equation between the molecular weight of the polymers and the pore size parameters of the metal–ceramic support; that is, the non-crosslinked polymer did not fill up or passed through the pores of the metal–ceramic support.

Despite the permeability reduction, the crosslinked polymers maintained the gas-separation properties of the noncrosslinked polymers (Table V; e.g., the permeability of C_4H_{10} was greater than the permeability of N_2). On the other hand, these polymers had separation selectivity toward He/N_2 mixtures at a level of 8–20, which is unusually high for elastomers. The raised separation selectivity obtained for O_2/N_2 (3–4) and for CO_2/CH_6 (>9), in comparison with PDMS, also had to be noted.

All the aforementioned permeability properties allow us to mention the unique potential of PVADMS polymers, especially if we take into account the easy preparation of thin membranes, without the need of any additives for crosslinking, and the good mechanical properties. On the whole, the permeability of these new organosilicon-containing elastomers exceeds the permeability of carbon-based rubbers, being inferior only to that of PDMS.

Effect of the time and temperature of the thermal treatment on the permeability parameters

As shown in Figure 9, the crosslinking induced by the thermal treatment resulted in a nonlinear decrease in the permeability of the inorganic gases down to about one order (except for He, which was 3 times only), whereas the permeability of C_2–C_7 hydrocarbons decreased 10–20 times. This tendency could probably be attributed mainly to the reduction of the diffusion coefficients: the crosslinking increased the diffusion resistance within the polymer matrix, and so the permeability of larger C_2–C_7 molecules was more severely altered. The preferable permeability for hydrocarbons was retained even after the complete crosslinking of the PVADMS structure. As shown in
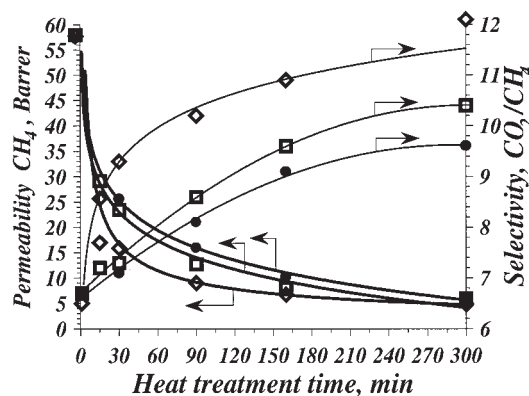
Figure 9 Dependence of the permeability of CH_4 and the selectivity for CO_2/CH_4 in PVADMS on the thermal treatment time: (●) 120, (□) 140, and (◇) 160°C.
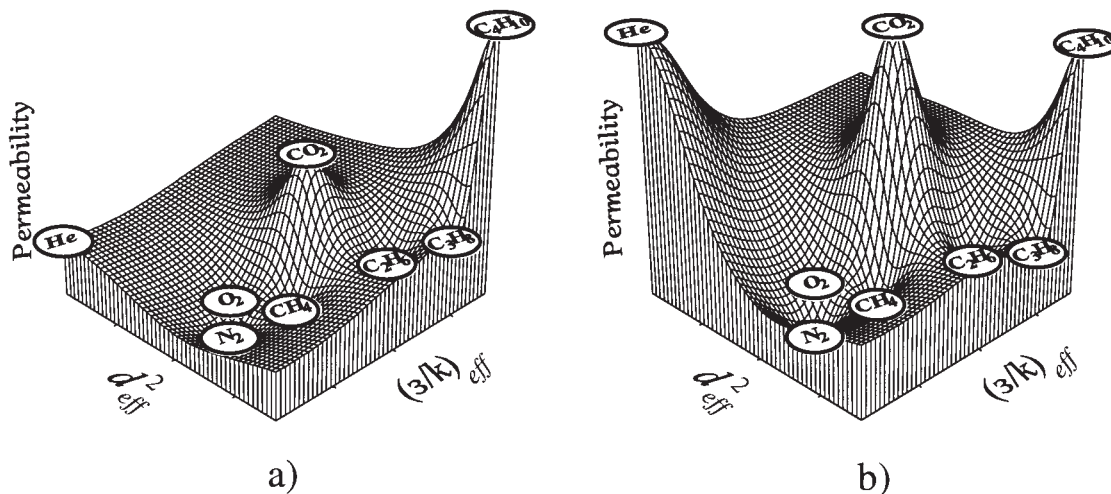
Figure 10 Relief of the permeability selectivity for some gases in (a) noncrosslinked PVADMS and (b) crosslinked PVADMS.

Figure 10, the permselective relief was calculated for noncrosslinked and crosslinked PVADMS samples with an approach based on the Lennard–Jones force constant and gas-molecule diameter.[11] The separation selectivity of PVADMS could be controlled by the crosslinking conditions. The crosslinked polymer exhibited preferable permeability for hydrocarbons, CO_2, and He and, therefore, could be used with these kinds of complex gaseous mixtures, particularly for petrochemical process streams.[19]

CONCLUSIONS

The permeability parameters of inorganic gases and hydrocarbons in a new class of polyorganosilicon-containing elastomers (PVADMS) containing unsaturated bonds within a mixed carbo-heterochain structure based on VADMS were systematically studied; in particular, the structure–property relationships were investigated with respect to the crosslinking extent of the PVADMS structure induced by a thermal treatment versus the time. The cis-CH≡CH— groups were preferentially oxidized, and this gave rise to peroxide bond formation at the beginning of the thermal treatment in air and led in turn to the formation of interchain oxygen-containing connections and finally to crosslinked macrochains.

PVADMS had higher permeability for C_1–C_4 hydrocarbons than for inorganic gases, regardless of its crosslinking extent. Moreover, the permeability for hydrocarbons increased with an increase in the number of carbon atoms in the hydrocarbon molecules up to more than one order of magnitude.

The permeability of the inorganic gases and C_1–C_4 hydrocarbons decreased nonlinearly with an increase in the crosslinking. The decrease in the permeability could be divided into two kinetic parts, fast and slow; the sharp decrease in the permeability of the gases correlated with the fast disappearance of the flexible cis-CH≡CH— structure in the polymer.

These new polymers based on VADMS are promising materials for the preparation of highly permeable selective membranes for the recovery of butane and other hydrocarbons from various chemical and petrochemical process streams. The obtained dependence of the gas permeability parameters on the crosslinking conditions (the temperature and time of thermal treatment) and the molecular weight of noncrosslinked polymers may be useful for formulating composite membranes with good resistance toward organic attack and profitable gas permeability parameters.

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