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Chlorination of Poly[(1-trimethylsilyl)-1-propyne] Membrane

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ABSTRACT: A characterization of poly[(1-trimethylsilyl)-1-propyne] (PTMSP) membranes treated with chlorine water is presented. PTMSP chlorination was carried out by dipping a PTMSP membrane in chlorine water at 25 °C. X-ray microanalysis reveals that after treatment the chlorine amount is relevant in the whole section of membranes and that the chlorine concentration increase is balanced by the silicon concentration decrease. Pristine PTMSP and chlorinated PMSTP vibrational spectra allow to suppose that in the macromolecule "special sites" are present which may be preferentially attacked by chlorine. A chlorination reaction scheme is given here.

Introduction

Poly[(1-trimethylsilyl)-1-propyne] (PTMSP) is a polymer characterized by a very high permeability to gases as shown by its permeability values to nitrogen and oxygen at 298 K, i.e., 3.4×10^{-7} and 6.1×10^{-7} cm^3 (STP) cm/(s cm Hg cm^2), respectively.[1] Permeability changes with history of the polymer and with physical aging. A recent paper[2] gives permeability values comprised in the range $(1.5-4.97) \times 10^{-7}$ and $(2.6-7.73) \times 10^{-7}$ for oxygen and nitrogen, respectively. This behavior makes PTMSP a very interesting polymer for possible use in membranes to separate gas mixtures.[1] Differential scanning calorimetry curves (DSC) show that PTMSP has no transition phase, and exothermic decomposition of this material starts in nitrogen at 573 K. Moreover, permeability to gases decreases with time while an increase of polymer density is observed.[3,4] This suggests that a physical aging of the polymer takes place with a rearrangement of possible configurations. To obtain a stabilization of the structure and of the transport properties, many authors studied PTMSP chemical modifications and modified materials properties.[5−8] In ref 8 modification of a PSTP membrane surface by fluorination is presented. The new membrane was characterized by almost constant transport properties over an extended period of time. Other authors[7] brominated PTSP by immersing a membrane in bromine water. Bromination is not limited to surface and takes place also in the membrane bulk. The aim of this paper is a study of chlorination of a PSTP membrane by immersing in chlorine water. Direct chlorination of the membrane allows taking immediately permeability tests on the modified membrane.

In this work we focus on the study of double-bond reactivity in a chlorination reaction. Reactive sites can be identified by using IR and FT-Raman spectroscopy and X-ray microanalysis system. Moreover, we suggest a scheme of chlorination reaction based on the experimental data obtained.

Experimental Section

Materials. Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) was obtained following the procedure indicated by Masuda et al.[1] by heating at 80 °C, in a nitrogen atmosphere, the monomer and the catalyst $TaCl_5$ dissolved in dry toluene. After 3 h, the polymerization was terminated by addition of a methanol−toluene mixture (1:10 volume ratio), and the polymer was separated by pouring its solution into an excess of methanol. The precipitated polymer was filtered, washed several times with hot methanol, and dried to a constant weight under reduced pressure at 50 °C.

Membranes were obtained from 3% polymer solutions in tetrachloroethylene by slow evaporation of solvent at room temperature. The average thickness is 200 μm, and the polymer average density is 0.8325 g cm^{-3}. Density is that measured before chlorination. The polymer intrinsic viscosity is 2.25 dL/g. The molecular weight is 298 000 Da determined according to[1] $[\eta] = KM^a$ where $K = 4.45 \times 10^6$ and $a = 1.04$.

Treatment with Chlorine Water. Chlorine water was prepared by saturation of deionized water with gaseous Cl_2. Chlorine was obtained by reaction between hydrochloric acid and potassium permanganate. The chlorine amount in water was determined iodometrically. The analysis result shows that chlorine content is 0.276 g in 100 g of chlorine water at room temperature.

Chlorination of the sample was carried out by immersion of a PTMSP film in chlorine water at room temperature. While chlorination was occurring the initially transparent and yellow film became opaque without any change of color. After 21 h this contact was interrupted. Then the membrane was washed with water and dried under reduced pressure to a constant weight.

Methods of Characterization. The intrinsic viscosity $[\eta]$ of polymers was measured in toluene solution at 30 ± 0.2 °C with an Ubbelhode viscosimeter. Density of the samples was determined by the analythic balance Sartorius YDK density kit.

Thermal analysis was performed on Mettler 3000 DSC instrument, under nitrogen atmosphere, with a scanning rate of 10 °C/min, in a temperature range from −150 to 400 °C.

Scanning electron microscopy (SEM) of membranes was carried out using a Cambridge Stereoscan 360 microscope; X-ray microanalyses were performed using the energy dispersion system Link AN 10000 Super, equipped with a (Si−Li) detector with a beryllium window. This window cannot detect elements with atomic number lower than 10. The accuracy of data from X-ray method is better than 4%.

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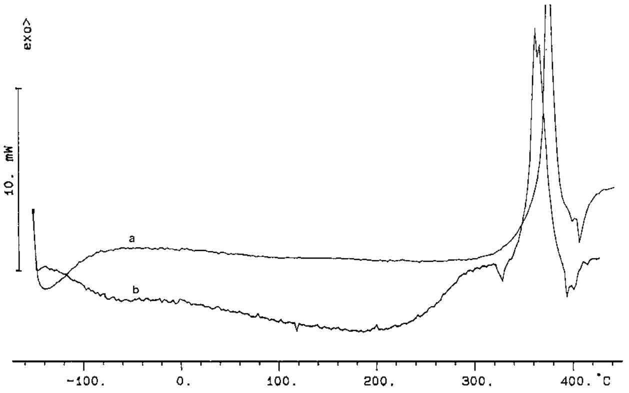


Figure 1. DSC analysis of pristine PTMSP (plot A) and of chlorinated PTMSP (plot B).

Table 1. Chemical Composition in Five Regions of a Flattened Section of Chlorinated PTMSP Film Thickness

microanalysis	% Si	% Cl	% Ta
10 µm from edge A	56	34	9.7
125 µm from edge A	78	8.7	12.8
in the center of the section	78.6	9.4	11.9
125 µm from edge B	79	9.2	11.6
10 µm from edge A	65.4	26.5	8

Infrared spectra were recorded on a Nicolet 7000 FTIR spectrophotometer in the region between 400 and 4000 cm^{-1} with 1 cm^{-1} resolution. Solid samples were analyzed in KBr pellets.

Raman spectra were recorded (in the range 400−3500 cm^{-1}) on a Nicolet 910 FT- Raman instrument, equipped with a Nd: YAG laser (λ_{exc} = 1064 nm). The excitation power was 0.45 W. No preparation was required for Raman experiments on solid samples. The spectra resolution was 1 cm^{-1}.

Results and Discussion

1. Chemical−Physical Properties of Modified Polymer. In comparison to starting PTMSP films, chlorinated membranes show the same solubility (in common solvents) but different values of intrinsic viscosity and polymer density.

The observed decrease of intrinsic viscostity [η] from [η] = 2.25 dL/g for the pristine polymer to [η] = 0.83 dL/g for the chlorinated sample suggests that along with chain modifications chain breaking also takes place. Because of the exponential relationship between [η] and M, a few chain breakings have a relevant influence on intrinsic viscosity.

Chlorinated PTMSP samples density increases 10%, passing from 0.8325 g cm^{-3} in unmodified polymer to 0.9191 g cm^{-3} in treated samples. This increase can be ascribed to a better packing of macromolecular chains, probably due to the local changes of the chain conformation after polymer chemical modifications. Chlorine chemical insertion may also increase density.

PTMSP is a thermoplastic, amorphous polymer, but it shows a peculiar thermal behavior.

DSC analysis (curve a, Figure 1) does not show any glass transition up to 300 °C. At this temperature, exothermic decomposition of sample takes place. These experimental data are clear evidence of polymer rigidity. The polymer structure is so stiff that, by thermal energy supply, it is easier to break primary bonds than to achieve rotational mobility.[2] On the contrary, in the DSC plot of the chlorinated membrane (curve b, Figure 1) one phase transition appears at 90 °C and exothermic decomposition begins at 200 °C, 100 °C below the pristine polymer decomposition temperature, and shows a maximum at about 365 °C. All differences observed indicate that, as a consequence of chlorine treatment, the system acquires some flexibility and polymer chains reach some mobility (due to cooperative torsional motions) before chemical decomposition.

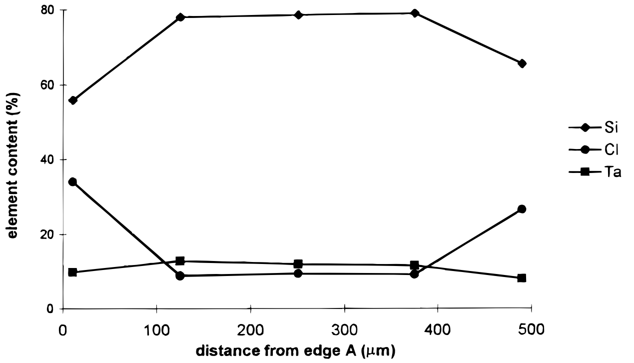


Figure 2. Variation of chemical composition vs distance from the edge "A" of a section of the treated PTMSP film thickness.

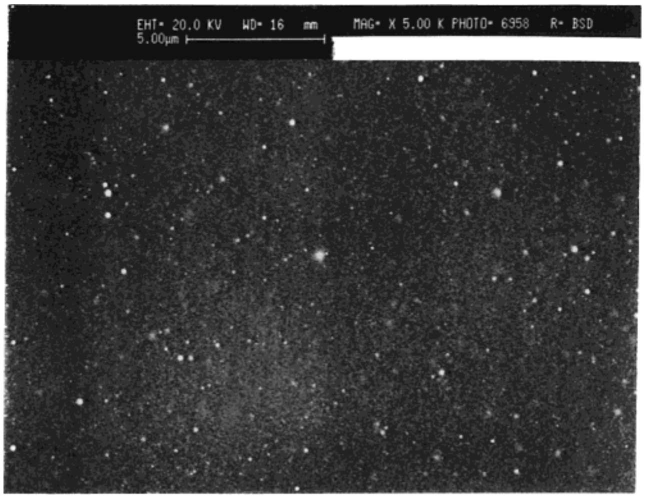


Figure 3. SEM micrograph of an untreated PTMSP surface.

Chlorine content in the membrane after treatment is 6 wt % (elemental analysis). Chlorine presence was confirmed by microanalysis with an X-ray probe combined with scannig electron microscopy, which allows obtaining both qualitative and quantitative information about elements with atomic number greater than that of sodium.

X-ray analyses of the chlorinated film, which according to SEM images looks like the pristine sample from the morphological point of view, provides percentages in chemical composition. It also provides important information on the chlorine distribution inside the polymer film. In fact, five microanalyses were performed in five different regions at different distances from edges A and B of a flattened section of sample thickness. Results are reported in Table 1 and are shown in the plot of Figure 2.

Percentages obtained are apparently very high due to the fact that this technique does not detect the presence of carbon and hydrogen atoms and shows the presence of chlorine, silicon, and tantalum in the membrane. Tantalum residues are not surprising, since tantalum is present also in the starting PTMSP. Figure 3 shows a SEM micrograph of the untreated PTMSP surface where some circular light regions appear on the dark matrix. Microanalysis of dark and of light regions (Figure 4) suggests that tantalum is present in both

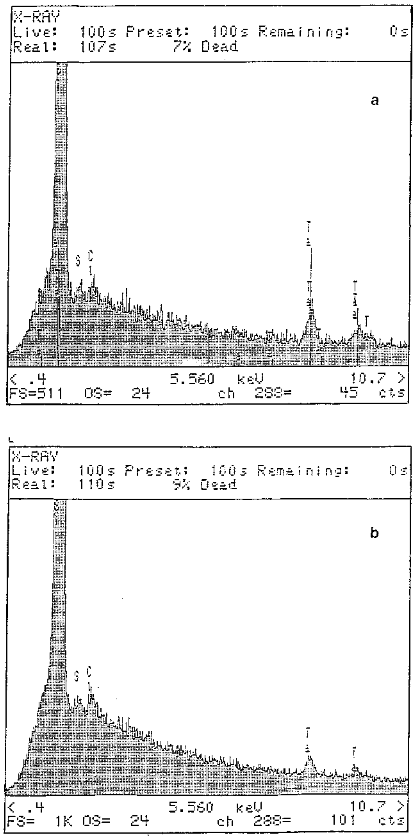


Figure 4. X-rays microanalysis of dark (a) and of light (b) regions of an untreated PTMSP sample.

domains, but its amount is higher in the light one. Obtained results indicate that several inclusions of tantalum with an inhomogeneous distribution are present in the PTMSP membrane; these inclusions could come directly from the initial solution which is supposed not to be perfectly homogeneous. Polymer solution microscope analysis revealed indeed the existence of microgels with an average diameter of 285 nm.

Table 1 and Figure 2 show that chlorine content decreases from surface to the inner of the membrane as is expected from a heterogeneous reaction depending on the reagent diffusion velocity. However, the chlorine amount is relevant in the whole section, and it suggests that the chlorination process not only concerns the membrane surface in direct contact with reagents but also involves the polymer whole bulk.

Moreover, results indicate that chlorine concentration increase moving from the middle of the section to the edges of our sample is balanced by a decrease in silicon concentration. This suggests that chlorine insertion in the chain being accompanied by silicon displacement, in agreement with the reaction mechanism discussed in section 3.

2. Analysis of Vibrational Spectra. Band assignment of PTMSP vibrational spectra is very helpful to clarify the origin of the few changes found in the infrared and Raman patterns of a PTMSP sample after treatment with chlorine water. (Infrared and Raman spectra of PTMSP and of the chlorinated sample are reported in Figures 5 and 6.)

To this aim correlations were established between vibrational frequencies and intensity patterns observed in PMTSP spectra and in those of some simple model compounds, where a reliable vibrational assignment is reported in the literature (see Table 2). Indeed, the nature of PTMSP vibrational modes is mainly localized, as if every structural unit were a small molecule with weak interactions with the adjacent units. This will be proved by several nice correspondences observed among polymer vibrational frequencies and those of the small molecular models. Moreover, all vibrational bands show simultaneous infrared and Raman activity. This is evidence that the polymer structure does not admit inversion center of symmetry operation, as expected of an amorphous polymer with very hindered structural units, where even short-range conformational order is unlikely.

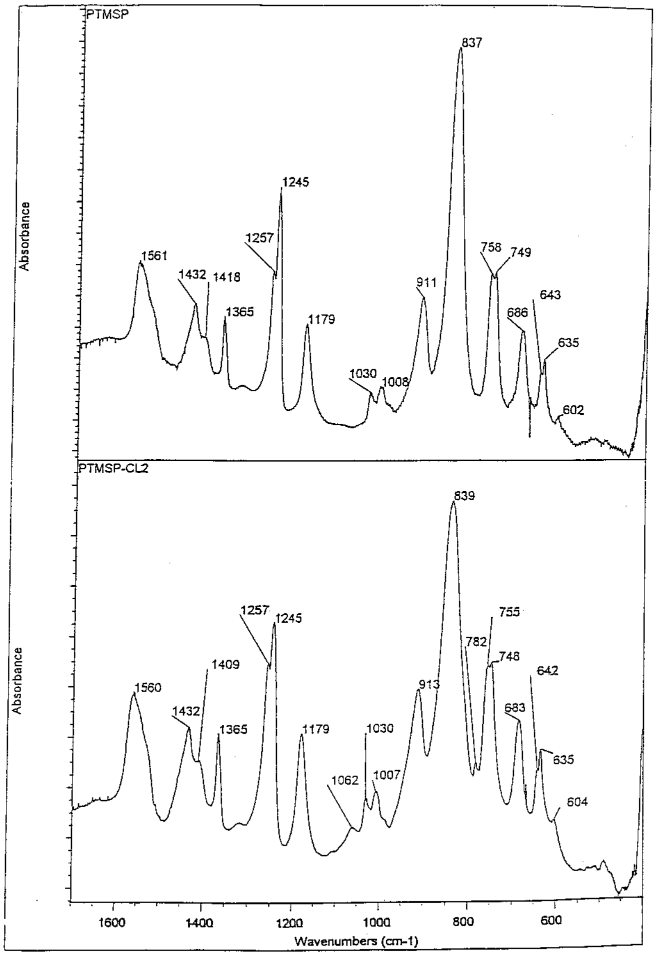


Figure 5. Infrared spectra of PTMSP: pristine (top) and chlorinated (bottom).

Vibrational group frequencies localized on the Si-$(CH_3)_3$ group have been identified by comparison with vibrational assignments[9] for trimethylsilane and tetramethylsilane (Table 2); frequencies characteristic of the methyl group directly attached to the C=C double bond can be found by comparison with propylene spectra[10] (see Table 2).

The simplest molecular model that can mimic the PTMSP structural unit is vinyltrimehylsilane (VTMS). Infrared and Raman spectra of VTMS commercial sample were recorded in our laboratory; a simultaneous assignment of the relevant bands observed in VTMS and PTMSP (reported in Table 3) was effected on the basis of correlative criteria by comparison with $Si(CH_3)_3H$, $Si(CH_3)_4$, and propylene.

The assignments proposed for pristine polymer spectra (see Table 3) are the following.

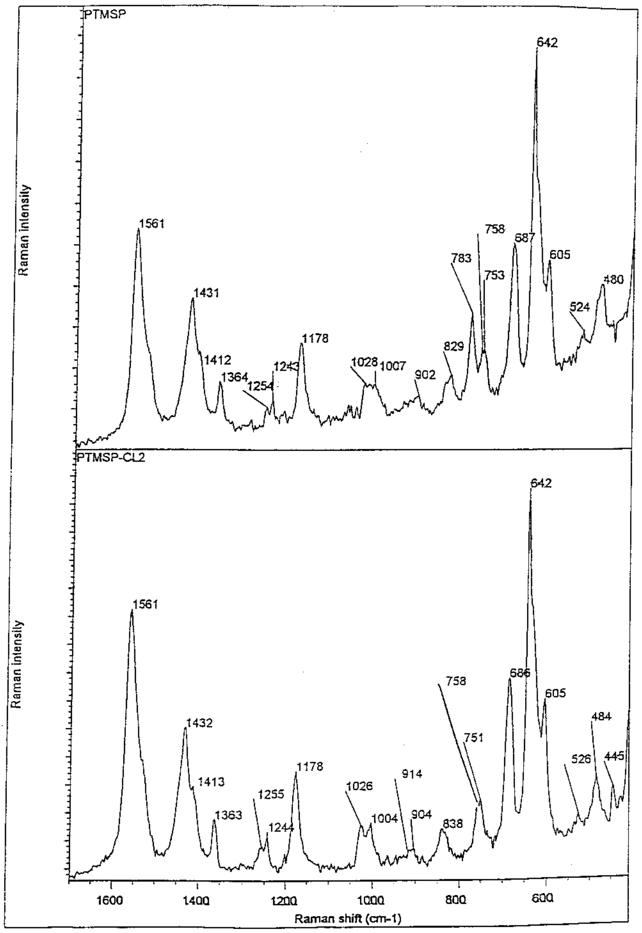


Figure 6. Raman spectra of PTMSP: pristine (top) and chlorinated (bottom).

CH stretching modes localized on the $Si(CH_3)_3$ group and on the “isolated” methyl group are responsible for bands between 2998 and 2905 cm^{-1}.

The strong band at 1561 cm^{-1} (observed in both infrared and in Raman spectra) is unequivocally assigned to the C=C stretching vibration, which occurs at very low frequency if compared, for instance, with that of propylene or ethylene, which is well above 1600 cm^{-1}.

By comparison with VTMS (where C=C stretching band is observed at 1595 cm^{-1}), one can argue that some conjugation takes place between π electrons of the double bond and electrons of the Si atom. As a consequence of conjugation, the C=C stretching frequency shifts downward and strong infrared activity arises, due to polarization of the C=C bond. On the other hand, because of the sterical hindrance of the $Si(CH_3)_3$ group, even short sequences of C=C double bonds cannot be on the same plane: this fact prevents the conjugation of C=C bonds along the polymer backbone in agreement with evidence from UV−vis spectra.[11]

Assignments in the region 1432−1245 cm^{-1} (see Table 3) and of the very strong infrared band at 837 cm^{-1} can be done simply by analogy with model compounds (Table 2).

Some PTMSP bands (1179, 1030, 1008, and 911 cm^{-1}) do not have a counterpart in the small model compounds and in VTMS: for this reason they should be assigned to some skeletal modes involving stretching of CC single bonds in the chain and in the isolated methyl group. (See also frequencies and vibrational assignment of propylene in this spectral region.)

Table 2. Vibrational Frequencies and Bands Assignment for Model Compounds (Data from Refs 9 and 10)[a]

trimethylsilane liquid		tetramethylsilane liquid		propylene liquid	
ν(Raman)	vib assignt	ν(Raman)	vib assignt	ν(Raman)	vib assignt
				3086	
				3015	q(=CH)
				3002	
				2990	
2964	q(CH)	2966	q(CH)		
		2957	q(CH)	2956	$q(CH)_{ME}$
				2924	$q(CH)_{ME}$
2900	q(CH)	2900	q(CH)		
				2870	
				1648	q(C=C)
				1448	$\alpha(HCH)_{ME}$
		1418	α(HCH)		
1411	α(HCH)	1416	α(HCH)	1415	$\alpha\ (HCH)_{ME}$
				1378^b	$\alpha(HCH)_{ME}$
				1297	β(C=C−H)
1263	α(HCH)	1263	α(HCH)		
1253	β(HCSi)	1250	β(HCSi)		
				1171^b	β(C=C−H) q(C−C)
				1045^b	β(C−C−H) γ(CH)
				991^b	τ(C=C) γ(CH)
				963^b	β(C−C−H)
				920	q(C−C) β(C=C−H)
				912^b	$\gamma(CH_2)$
853	β(HCSi)	859	β(HCSi)		
831	β(HCSi)	829	β(HCSi)		
711	q(SiC)	694	q^-(SiC)		
624	q(SiC)				
		593	q^+(SiC)		
				580	γ(CH)
				430	ω(C=C−C)

[a] Symbols used: q = stretching vibration; α(HCH) = bending vibration of valence angle HCH; β(HCX) = bending vibration of valence angle HCX, X = C, Si; γ = out-of-plane bending; τ = torsional vibration. [b] Infrared, gas.

A deeper attention must be paid to the spectral zone between 800 and 500 cm^{-1}, where characteristic modes involving Si−C stretching vibrations occur.

In the $Si(CH_3)_3H$ molecule we find two bands (at 711 and 624 cm^{-1}) which are assigned to the asymmetric (E symmetry species, doubly degenerate) and to the symmetric (A_1 species) stretching vibrations of Si−C bonds, respectively. The VTMS lower symmetry removes the degeneracy of E modes and gives rise to a triplet of bands at 692, 673, and 584 cm^{-1}, which can be assigned to the same kind of vibrations mainly localized on the $Si(CH_3)_3$ group. In the same spectral region, a new band at 756 cm^{-1} appears in VTMS, which can be reasonably ascribed to a vibration which mainly involves the stretching of the Si−C bond linked to the C=C double bond. The increase in frequency with respect to stretching vibrations localized on the $Si(CH_3)_3$ group can be rationalized in terms of conjugation between Si atom and the π bond, which is responsible for an increase of the bond order of Si−C bond and of its stretching frequency.

In the same region (between 783 and 602 cm^{-1}) we find many peaks in the polymer spectrum. We can observe at least eight different frequencies in this range, which can be divided into two main groups. They can

Table 3. Vibrational Frequencies and Bands Assignement for PTMSP, Chlorinated PTMSP, and VTMS (See Text)[a]

PTMSP		PTMSP-Cl$_2$		VTMS		
ν(IR)	ν(Raman)	ν(IR)	ν(Raman)	ν(IR)	ν(Raman)	vib assignt
				3050	3049	q(=CH)
				3011		q(=CH)
	2998		2995			q(CH)$_{ME}$
2989		2981		2963	2964	q(CH)$_{ME}$
2958	2957	2960	2957	2959		q(CH)$_{ME}$
2907	2905	2905	2904	2898	2896	q(CH)$_{ME}$
		2850				q(CH)$_{ME}$
1561	1561	1560	1561	1595	1594	q(C=C)
1432	1431	1432	1432			α(HCH)$_{1ME}$
1418	1412	1409	1413	1405	1405	α(HCH)$_{3ME}$
1365	1364	1365	1363			α(HCH)$_{1ME}$
					1272	α(HCH)$_{vinyl}$
1257	1254	1257	1255	1253		α(HCH)$_{3ME}$
1245	1243	1245	1244			β(HCSi)
1179	1178	1179	1178			q(C−C)
		1062				see text
1030	1028	1030	1026			q(C=C)
1008	1007	1007	1004			q(C=C)
				1008		γ(CH)
				952		γ(CH$_2$)
911	902	913	914			q(C−C)
			901			q(C−C)
837	829	839	838	857/835	834	β(HCSi)
	783					see text
		782				see text
758	758	755	758	756	756	q(SiC-chain)
749	753	748	751			q(SiC-chain)
686	687	683	686	692	691	q(Si−CH$_3$)
643	642	642	642	673	671	q(Si−CH$_3$)
635	*b*	635	*b*			q(Si−CH$_3$)
602	605	604	605		584	q(Si−CH$_3$)
	524		526	514		ω(C=C−Si)
	480		484			ω(C=C−C)
			445			see text

[a] See Table 2 for symbols used. [b] Shoulder.

be easily assigned by analogy with the VTMS molecule. In the higher frequency range we assign stretching vibrations which mainly involve C−Si bonds attached to the polymer chain. The appearance of different frequencies can be explained if we consider that along the polymer chain nonequivalent structural units can exist: they differ from one another because of configurations and various conformations in the chain.

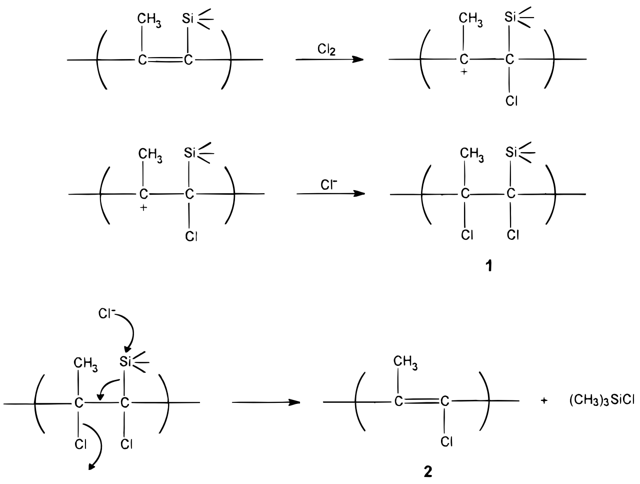
The low-frequency group of bands (683−602 cm^{-1}) can be assigned to Si−C stretching modes mainly localized on the Si(CH$_3$)$_3$ group, as in the VTMS spectrum.

In the lower frequency region we find two other bands which can be reasonably ascribed to skeletal deformation modes (see Table 3).

In the case of the polymer after treatment with chlorine water some small but clear differences can be observed: (i) The Raman peak at 783 cm^{-1}, clearly observed in the Raman spectrum of the pristine sample, completely disappears. (ii) In the infrared spectrum two new weak bands appear at 1060 and 782 cm^{-1}. (iii) A new peak at 445 cm^{-1} arises in the Raman spectrum.

According to a previous discussion, Raman frequencies at 783 cm^{-1} are assigned to a Si−C stretching vibration localized on a structural unit with a well-defined configurational and/or conformational environment.[18] The disappearance of this band after chlorination can be explained with the disappearance of some "special" sites (from the point of view of the structure) which have been preferentially attacked by chlorine. This interpretation is in good agreement with the reaction scheme proposed in section 3, which suggests that Cl substitutes a Si(CH$_3$)$_3$ group (responsible for the 783 cm^{-1} transition), which leaves the chain.

Scheme 1. Mechanism of the Chlorination Reaction



The fact that a new infrared band (observed in chlorinated sample) appears at the same frequency as the band which disappears in the Raman pattern is in our opinion completely fortuitous. Activation of a Raman transition in the infrared spectrum must be indeed explained in terms of a local symmetry lowering: this mechanism does not allow to justify the simultaneous disappearance of the same vibrational mode in the Raman spectrum. According to the above reasoning, we suggest that the new infrared peak at 783 cm^{-1} can be ascribed to a vibrational mode involving C−Cl stretching localized on the chemical defect introduced by treatment.

The second new peak observed in the infrared spectrum at 1060 cm^{-1} can be assigned to some vibrations involving the CH$_3$−C=C−Cl group. This interpretation is based on the comparison with a series of infrared spectra (reported in the literature[12]) of compounds that contain the CH$_3$−C=C−Cl group. For the new Raman band at 445 cm^{-1} we do not have, at the moment, a satisfactory assignment to propose.

3. Reaction Mechanism. The strong localization of π electrons and the consequent weak conjugation along the polymer backbone allow to consider PTMSP as a sequence of trisubstituted vinylsilane units, independent of one another.

Usually vinylsilanes react with electrophiles with either addition to the double bond or substitution of the SiR$_3$ group, but substitution is more common because of the ease of silicon displacement.[13] In particular, when the electrophile is a halogen, halogenodesilylation products are preferentially obtained.[13−16]

On the basis of the experimental data collected and by analogy with the typical reactivity of vinylsilanes, we think that the mechanism reported in Scheme 1 is the most probable for PTMSP chlorination. It consists of the initial formation of the dichloro adduct **1** followed by the elimination of trimethylchlorosilane with restoration of the double bond to give substitution product **2**.

In Scheme 1 we report only the β-silylcarboniun ion because a Si−C bond stabilizes preferentially the carboniun ion β to silicon for the hyperconjugative effect.[17]

The reaction mechanism proposed supports the results obtained from X-ray micronalysis of the membrane, and it is in agreement with the conclusion reached by vibrational spectra interpretation (see sections 1 and 2).

As a consequence of the loss of a bulky group as Si(CH_3)$_3$, the PTMSP chain could acquire some more rotational mobility. Moreover, the increase in density in the treated polymer should confirm the existence of units **2** (see Scheme 1) in the chain: sterical hindrance decrease, indeed, can promote a better interchain packing.

Since the reagent system is chlorine water, one can suppose that together with the main substitution product also halo alcohol can be formed. However, infrared spectra analysis does not support this hypothesis since in the region of the O−H stretching we do not observe new bands.

Conclusion

Characterization of a PTMSP membrane treated with chlorine water was performed by thermal analysis, X-ray microanalysis, and IR and Raman vibrational spectroscopy.

The combined use of these techniques allows to state that, in our experimental conditions, chlorine atoms do not react with the double bond in the chain. As a consequence of chlorination process, indeed C=C−Cl groups are present: they are formed by substitution of the trimethyilsilyl group. This idea is supported by X-ray data which clearly show that chlorine concentration increase in different areas of the membrane is balanced by silicon concentration decrease. Moreover, the disappearance of a specific Raman-active transition (783 cm^{-1}) after chlorination was ascribed to the disappearance of a (CH_3)$_3$Si group from a "special" site, preferentially attacked by chlorine.

DSC analysis of the pristine polymer does not show any transition below 300 °C. At this temperature exothermic decomposition of the sample takes place. On the contrary, the chlorinated polymer shows a phase transition at about 90 °C, and the decomposition begins at 200 °C, 100 °C below the pristine polymer decomposition. These differences indicate that, as consequence of the chlorination, the system acquires some flexibility.

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(18) Notice that this frequency does not appear in the infrared spectrum of PTMSP, at difference with all the other Raman transitions in the same spectral region.

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