Thermal oxidation of poly(1-trimethylsilylprop-1-yne) studied by IR spectroscopy

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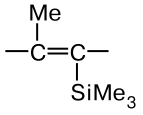
Thermal oxidation of poly(1-trimethylsilylprop-1-yne) was studied by IR spectroscopy in the 20—245 °C temperature interval. In the 20—160 °C temperature range, the reaction proceeds predominantly at the C—Me group as revealed by the decrease in the intensity of the bands of the methyl group bound to the C atom and the appearance of the bands of the hydroperoxide and methylene groups. The decomposition of hydroperoxides produces aldehydes and ethers. At 160—200 °C, oxidation occurs *via* two routes: at the C—Me and C=C groups, while the Me_3Si group remains unchanged. At 230—240 °C, the rate of the reaction occurring at the C=C bond is higher than the rates of the processes involving the MeC and Me_3Si groups. The relative content of the structural units was calculated for the samples oxidized at different temperatures. Plausible mechanisms of thermal oxidation of poly(1-trimethylsilylprop-1-yne) were considered on the basis of the data obtained.

Key words: poly(1-trimethylsilylprop-1-yne), thermal oxidation, IR spectroscopy.

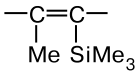
Poly(1-trimethylsilylprop-1-yne), $[—C(Me)=C(SiMe_3)—]_n$ (PTMSP), is characterized by very high parameters of selective gas permeability caused by the specific features of the macromolecule structure[1,2] and the morphology of amorphous polymer.[3,4] One of the advantages of PTMSP compared to other polyacetylene substituted derivatives is its higher stability toward oxidation in air.[5] However, mechanisms of thermal oxidation of PTMSP were not virtually studied. The thermal destruction of PTMSP and other polyacetylenes has previously been studied using TGA and IR spectroscopy with maintaining the temperature of the samples at 100—140 °C for 20 h *in vacuo* and in air.[5] The authors proposed a unified mechanism of thermal oxidative destruction of substituted polyacetylenes *via* the scheme of formation of hydroperoxides in the main chain during the interaction of the primary macroradical with the oxygen molecule and termination of the main chain to form the carbonyl and hydroxyl groups.

At the same time, the oxidation of poly(methylacetylene) in the presence of oxygen for 14 h at 60 °C results in the appearance of bands of the carbonyl and hydroxyl groups along with a decrease in the intensity of bands of the methyl group and the appearance of bands of the methylene groups in the IR spectrum.[6] It can be expected that the physical heterogeneity of glassy PTMSP and nonequivalence of structural elements provide conditions for the structural and kinetic heterogeneity of oxidation, which develops *via* different routes. Therefore, it was of interest to study the transformations of PTMSP during thermal oxidation using IR spectroscopy, which makes it possible to determine the localization of active sites and the sequence of chemical transformations in different reaction steps.

The monomeric unit in PTMSP (in the *cis*- and *trans*-configurations) has three types of groups, which can be involved in thermal oxidation: C=C, C—Me, and Si—Me.



trans



cis

The specific features of their reactivity resulting from the structure of the polymeric chain should be specially mentioned. The double bond in PTMSP is strongly shielded, and this should impede the access of oxygen. It is known that PTMSP is not a polyconjugated system.[1] Among the Me groups, the groups at the Si atom are least reactive. At the same time, the C—Me groups can be affected to a great extent, because their C—H bonds are in the allyl position with a significantly decreased energy.

Experimental

A PTMSP sample (T_c > 200 °C, [η] = 5.5 dL g^{-1}) with a random distribution of units in the *cis*- and *trans*-configurations

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in a ratio of 40 : 60 was synthesized with the $TaCl_5$—triisobutylalumoxane (TIBA) catalytic system and purified according to a previously described procedure.[7] IR spectra were recorded in the 4000—200 cm^{-1} frequency range using an AF-1 FTIR spectrometer (NTTs UP RAS) and a Specord M-80 spectrophotometer (Carl Zeiss, Jena). Temperature dependences of the spectra were taken in a constant-temperature cell in the 20—245 °C temperature interval with an accuracy of ±1 °C. Spectra were measured during thermal oxidation in an open cell with the free access of air to the sample. In order to take into account the influence of conformational transformations in the polymer on the temperature changes of the spectra, the measurements were carried out in the same temperature interval as that used for the evacuation of the cell. The values of the absorbance were determined in the maxima of absorption bands. Samples of the polymer under study were free films with a thickness from 10 to 40 μm obtained from solutions in benzene or toluene ($C = 0.5\%$) or pellets with KBr. The thickness of the PTMSP films was estimated from the absorbance of bands using the calibration data for the films with the thickness greater than 30 μm measured using a micrometer followed by extrapolation to the zero thickness.

Results and Discussion

When analyzing the IR spectra of the PTMSP films measured at a constant temperature in air, we can conventionally distinguish three temperature regions corresponding to different oxidation steps. The low-temperature region (from 20 to 60—80 °C) is characterized by the appearance of absorption bands of unstable oxidation products in the spectrum. The medium region (from 60—80 to 160—180 °C) is characterized by oxidation chain propagation, which occurs mainly at the C—Me group. At high temperatures (from 190 to 240 °C), oxidation is accompanied by the thermal decomposition of the polymer.

Low-temperature processes. The fragments of the nonoxidized TPMSP film and the products of oxidation at 230 °C are presented in Fig. 1. The first indications of TPMSP oxidation appear at 40—60 °C as weak bands in

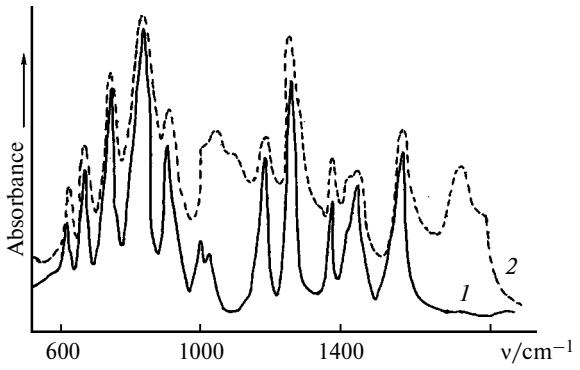

Fig. 1. IR spectra of the nonoxidized (*1*) and oxidized at 230 °C (*2*) PTMSP samples.

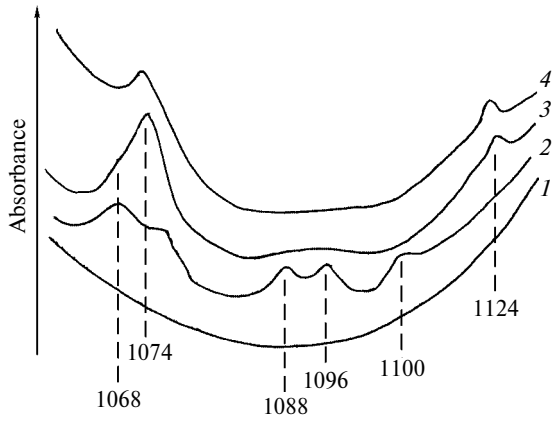

Fig. 2. IR spectra of the PTMSP films in the 1130—1050 cm^{-1} interval: nonoxidized (*1*) and oxidized at 70 (*2*), 150 (*3*), and 230 °C (*4*). The figures in the curves designate the frequencies of maxima in cm^{-1}.

the region of stretching vibrations of the hydroxyl groups, *viz.*, a very weak band at 3550 cm^{-1} and a weak band at 3380 cm^{-1} with a half-width of 120 cm^{-1}, and bands in the region of stretching vibrations of the C—O bond. The latter look like a broad low-intensity band with pronounced maxima at 1100, 1096, 1088, and 1068 cm^{-1}. The intensity of the band increases slightly on heating to 120—130 °C, after which two bands with the frequencies 1124 and 1074 cm^{-1}, which are assigned to vibrations of the ether groups, are formed instead of the broad band. The transformation of the broad band at 1130—1050 cm^{-1} in the oxidation steps under study is presented in Fig. 2. These spectra characterize the thermal stability of the ether groups with absorption bands at 1124 and 1074 cm^{-1}, which are observed in the spectrum at temperatures below 220 °C. Evidently, the broad band at 1130—1050 cm^{-1} can be attributed to unstable intermediates containing C—O bonds. These compounds can be peroxide radicals and hydroperoxide groups. The time interval, during which the band is observed in the spectrum (180 min), is too long for the short-lived peroxide radicals. Polymeric hydroperoxides are usually identified only by bands of stretching vibrations of hydroxyl groups. In the study of polypropylene hydroperoxides, the bands at 3550 cm^{-1} and 3380 cm^{-1} (the latter with the half-width 150 cm^{-1}) were assigned[8] to vibrations of the free hydroxyl groups and those bound by intramolecular H bonds, respectively. Bands of the ν(OH) vibrations of polymeric hydroperoxides are weak and localized in the absorption region of the OH groups of alcohols. Therefore, the weak bands at 3550 and 3380 cm^{-1} observed in the spectrum of PTMSP can presumably be assigned to vibrations of hydroperoxides. The medium region of the IR spectrum of low-molecular hydroperoxides contains the characteristic bands near 850 cm^{-1} and in the 1060—1120 cm^{-1} interval.[9] The first of these bands in the spectrum of PTMSP overlaps with a

very intense band at 848 cm^{-1} (ρ(SiMe)) (see Fig. 1), and the second band corresponds to the position of the broad band at 1130—1060 cm^{-1}. For example, the spectrum of cyclohexene hydroperoxide contains the bands with frequencies of 1096 and 1068 cm^{-1},[9] coinciding with the maxima of the band at 1130—1060 cm^{-1}.

Thus, the spectral changes observed in the low-temperature region of oxidation are related to the appearance of valence-saturated but unstable structural groups resembling in their spectroscopic properties to both free hydroperoxide groups and those bound by intramolecular H bonds.

At ~80 °C, the bands of the methylene groups at 1375, 1465 (δ(CH_2)), 2926 (ν^{as}(CH_2)), and 2875 (ν^{s}(CH_2)) cm^{-1} appear in the spectrum. The latter is characteristic of the —CH_2—O— group.

Thermal oxidation at medium temperatures. At temperatures higher than 140 °C, when the decomposition rate of hydroperoxides is high, the bands at 1096 and 1088 cm^{-1} are virtually not observed (see Fig. 2, curve *3*). The bands of the aldehyde group at 1734 cm^{-1} (ν(C=O)) appear simultaneously with the bands of the ether groups at 1074 and 1124 cm^{-1} in the medium temperature region. In the same temperature interval, the intensity of the bands of the C—Me group decreases and the intensity of the bands of the methylene groups increases. The fragments of the spectra of the nonoxidized (curve *1*) and oxidized at 80 and 140 °C for 1 h (curves *2* and *3*) films and the differential spectra obtained by the subtraction of the first spectrum from the second and third spectra (curves *4* and *5*) are presented in Fig. 3. The spectra were measured at room temperature. These spectra characterize the increase in the content of the methylene groups in the medium temperature region (the bands at 1375, 1465, 2926, and 2875 cm^{-1}).

The temperature dependences of the spectroscopic characteristics of the PTMSP films with the thickness 30 μm in the 20—200 °C interval, which covers the low-temperature, medium, and partially high-temperature regions, are presented in Fig. 4. The measurements were carried out at the rate of temperature change 0.5 deg min^{-1}. The curves in Fig. 4, *a* were obtained upon two successive cycles of heating the samples at an interval of 20 days followed by cooling. The content of the oxidation products, *viz.*, aldehyde and ether groups (the bands at 1734 and 1074 cm^{-1}, respectively), increases on the first heating. The intensity of the band at 1734 cm^{-1} increases insignificantly after cooling to 20 °C followed by storage in air and after the repeated heating and cooling. The intensity of the band at 1074 cm^{-1} increases only on the first heating and is not observed on the second heating and cooling of the sample.

The intensities of the bands of the Me_3Si group remain unchanged after heating to 200 °C, experiencing only weak reversible changes related, most likely, to the temperature dependences of the density of the substance. Figure 4, *b* presents the data for the bands at 686 and 636 cm^{-1} (ν(SiMe)) (curves *3* and *5*, respectively). No decrease in the intensity was observed for bands of other vibrations of the Me_3Si group (the bands at 758, 838, and 1252 cm^{-1}). These facts indicate the thermal stability of the Me_3Si group in this temperature interval. Therefore, the bands at 686 and 636 cm^{-1}, whose intensities are comparable with the bands of the oxidation products, were chosen as an internal standard for measurements at temperatures not higher than 220 °C.

The spectroscopic parameters of the bands of the C—Me group and double bond exhibit a more complicated temperature dependence. As can be seen from the data in Fig. 4, *b*, the intensities of these bands decrease

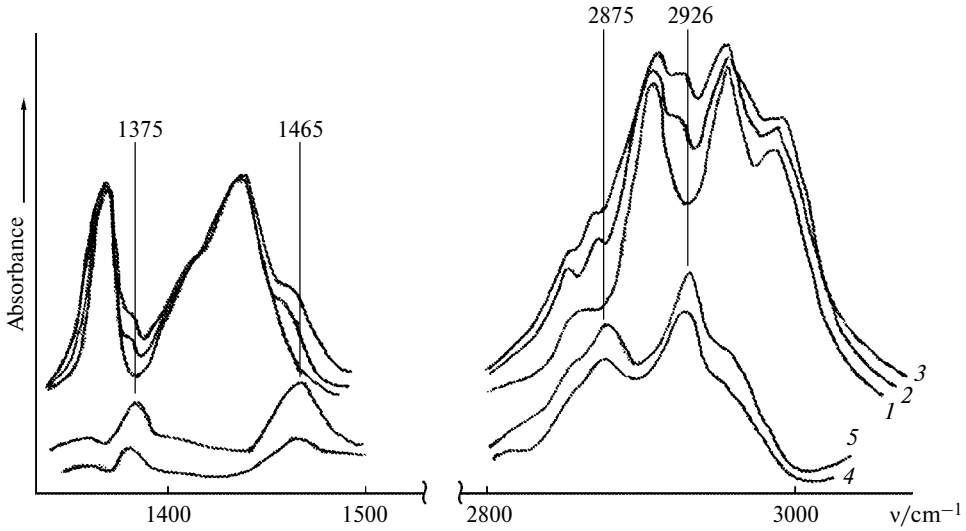

Fig. 3. Fragments of the spectra of the PTMSP films: nonoxidized (*1*), oxidized at 80 (*2*) and 140 °C for 1 h (*3*); differential spectra obtained by the subtraction of the first spectrum from the second (*4*) and third spectra (*5*).

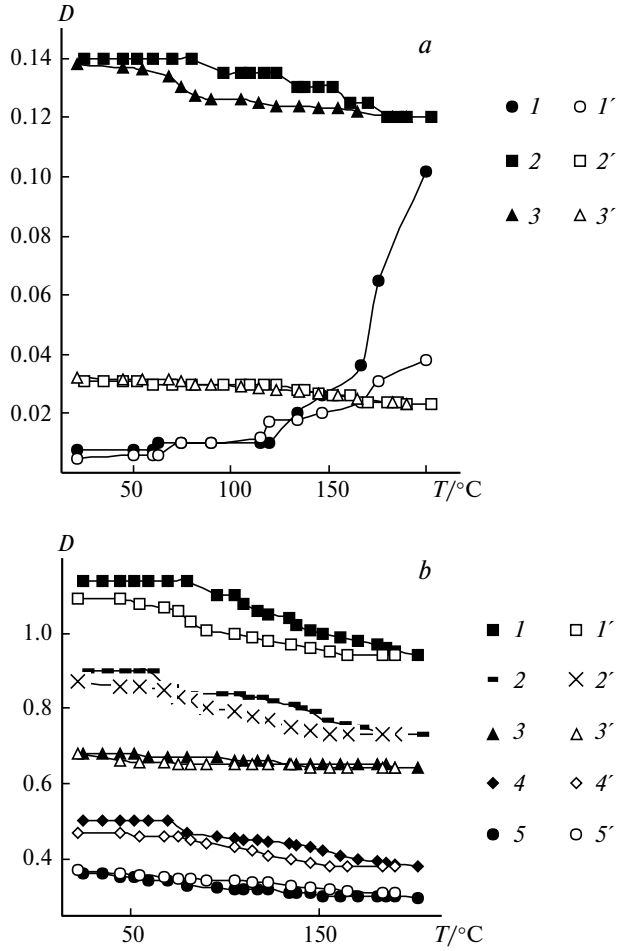

Fig. 4. Temperature plots of the absorbances of bands in the IR spectra of the PTMSP film: (*a*) bands at 1734 (*1*—*3*) and 1074 cm^{-1} (*1′*—*3′*) on the first (*1*, *1′*), second heating (*2*, *2′*) and cooling (*3*, *3′*); (*b*) bands at 1560 (*1*, *1′*), 1180 (*2*, *2′*), 686 (*3*, *3′*), 1364 (*4*, *4′*), and 636 cm^{-1} (*5*, *5′*) on heating (*1*—*5*) and cooling (*1′*—*5′*).

after heating to 200 °C. The intensities of the bands of the C—Me group with frequencies of the maxima of 1180 cm^{-1} (ρ(Me), ν(C—Me)) and 1364 cm^{-1} (δ(Me)) change substantially in the 80—200 °C temperature interval. The maxima are shifted simultaneously by 10 cm^{-1} (1180 cm^{-1}) and 2 cm^{-1} (1364 cm^{-1}). Similar changes in the spectroscopic parameters are observed for the band at 1560 cm^{-1} assigned to the ν(C=C) vibrations. All three bands consist of several components, and the ratio of their intensities changes in the same temperature interval. These changes are reversible and can be reproduced in the subsequent heating—cooling cycles and when the experiment is carried out in an evacuated cell. Most likely, the spectroscopic parameters of these bands are determined by the configurational heterogeneity of the polymeric chain and by the internal rotation about the C—C bonds.

The relative content of structural elements of the PTMSP samples oxidized for 60 min at 160, 180, and 220 °C is presented in Table 1. The consumption of the C—Me groups upon oxidation is characterized by a decrease in their content relatively to the more stable elements of the PTMSP structure, namely, the Me_3Si group and the double bond. As can be seen from the data in Table 1, in the samples oxidized at 180 and 220 °C, the decrease in the content of the C—Me groups relative to the Me_3Si group is greater than that relative to the double bond, which is accounted for by the partial oxidation of the latter. This corresponds to the appearance of a weak band at 1270 cm^{-1}, which can be assigned to vibrations of the epoxide groups. The higher relative content of the Me groups measured using the band at 1364 cm^{-1} over that measured at 1184 cm^{-1} can be explained by the overestimated D_{1364} value due to the contribution of the methylene groups at 1375 cm^{-1}.

Thus, the data in Table 1 and in Figs. 3 and 4 show that oxidation occurs mainly at the C—Me group and is accompanied by conformational transformations in the polymer. One of the oxidation products is the ether group characterized by the bands at 1124 and 1074 cm^{-1}, which lie in the region of the ν(C—O) vibrations of cyclic and linear ethers. Analysis of the published spectra of ethers suggests that these bands are attributed to vibrations of cyclic ethers, in particular, hydropyrans.[10,11] This assumption is supported by the following facts: the solubility of the PTMSP samples oxidized at temperatures below

Table 1. Relative content of the structural units* in the PTMSP samples** determined from different pairs of analytical bands (ν/cm^{-1})

T/°C	$\frac{C^{ox}_{C-Me} : C^{ox}_{Si-Me}}{C_{C-Me} : C_{Si-Me}}$		$\frac{C^{ox}_{C-Me} : C^{ox}_{C=C}}{C_{C-Me} : C_{C=C}}$		$C_{C=O} : C_{Si-Me}$	$C_a : C_k$	$C_l : C_k$
	(1364, 686)	(1184, 686)	(1364, 1560)	(1180, 1560)	(1717—1770, 636)	(1734, 1717)	(1770, 1717)
160	0.96	0.96	0.99	0.95	0.02	8.06	—
180	0.94	0.83	0.96	0.90	0.09	4.89	0.13
220	0.77	0.56	0.88	0.63	0.39	1.30	0.32

* C and C^{ox} are the concentrations of the groups before and after oxidation, respectively; C_a, C_k, and C_l are the concentrations of aldehyde, ketone, and lactone, respectively. The $C_{C=O} : C_{Si-Me}$ ratio was determined from the expression $D_{C=O}k_{636} : D_{636}k_{C=O}$, where D are absorbances, and k are molar absorption coefficients of bands.

** Oxidized for 60 min.

200 °C and the unchanged intensity of the bands at 1124 and 1074 cm^{-1} against the increase in the intensity of bands of other oxidation products. In fact, the formation of "internal" ethers is restricted by a combination of the configurational and conformational factors, which create conditions for the spatial orientation of the Me group favorable for the intramolecular occurrence of the reaction.

High-temperature oxidation. In the 190—220 °C temperature region, the spectra contain bands of the epoxide groups with frequencies of 1260 and 1230 cm^{-1}. This fact along with the decrease in the intensity of the band of the stretching vibration of the C=C bond relatively to the bands of the Me_3Si group indicates that the reaction occurs at the double bond. In the same temperature region at the unchanged intensity of bands of ethers (the bands at 1074 and 1124 cm^{-1} are present in the spectrum below 220 °C and then overlap with the intense band of the alcohol group at 1064 cm^{-1} with the simultaneous appearance of the ν(OH) band at 3410 cm^{-1}), the total intensity increases, and the absorption bands in the region of stretching vibrations of the carbonyl group are transformed. In addition to the absorption band of the aldehyde groups at 1734 cm^{-1}, the spectrum contains bands at 1717 and 1770 cm^{-1} attributed to ketones and γ-lactones, respectively. The composition of the carbonyl compounds at different stages of PTMSP oxidation is estimated in Table 1. The molar absorption coefficients of the ν(C=O) bands of different carbonyl compounds (products of the oxidation of polyolefins) were used in the calculation.[12] The temperature rise results in a decrease in the content of the aldehyde group and changes the composition of the carbonyl compounds in favor of ketones and γ-lactones (see Table 1). The presence of γ-lactones indicates a considerable role of the intramolecular reaction in the high-temperature region. The decrease in the content of the aldehyde groups with the temperature rise is related to their oxidation and degenerate branching of the process *via* Scheme 1.[13]

Scheme 1

$$P—CHO + O_2 \rightarrow P—CO^{\cdot} + HO_2^{\cdot}$$

$$P—CO^{\cdot} \rightarrow P^{\cdot} + CO$$

P is the fragment of the polymeric chain

The accumulation of the aldehyde groups and their decomposition with the formation of free radicals result in autocatalysis at high temperatures.

The kinetic curves obtained after fast (for 10 min) heating of the samples to 230 and 240 °C followed by keeping them at the constant temperature are presented in Fig. 5. It can be seen that the rate of consumption of

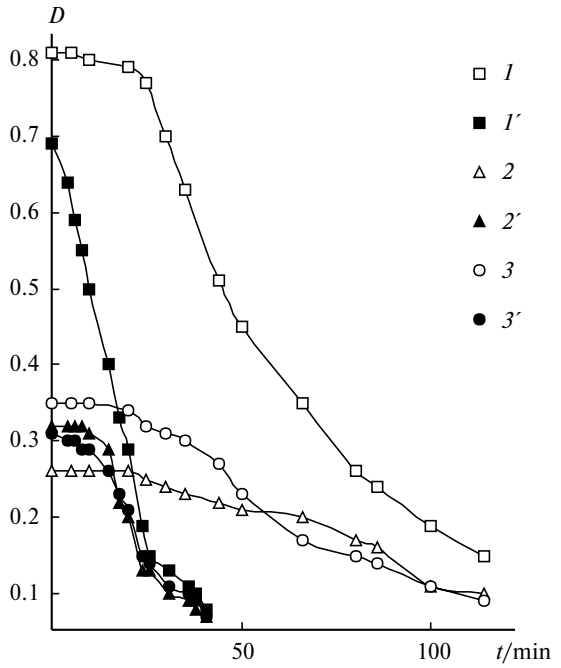

Fig. 5. Plots of the absorbances of absorption bands at 1560 (*1*, *1′*), 1364 (*2*, *2′*), and 636 cm^{-1} (*3*, *3′*) *vs.* time of oxidation of the PTMSP film at 230 (*1—3*) and 240 °C (*1′—3′*).

the C—Me groups (the band at 1364 cm^{-1}) and Si—Me group (the band at 636 cm^{-1}) is lower than that of the double bond (the band at 1560 cm^{-1}).

Thus, the high-temperature destruction occurs with a higher rate in the main chain. It is most likely that thermal decomposition and nonradical reactions, for example, hydrolysis, contribute substantially to this process. For example, the nonvolatile products of PTMSP oxidation at 230 °C contain silanol groups (the band at 3696 cm^{-1}) formed due to hydrolysis of the Me_3Si groups. The elimination of the substituents results in the appearance of the ν(C=C) bands with frequencies of 1648 cm^{-1} (nonconjugated alkenes) and 1600 cm^{-1} (fragments of the chain with polyconjugation). Oxidation products include alcohols detected in the spectrum by the ν(OH) band of the associated alcohol groups (3410 cm^{-1}) and the ν(C—O(H)) band with a maximum at 1060 cm^{-1} on the broad band at 1050 cm^{-1} (see Fig. 1, curve *2*). It is noteworthy that the content of alcohol groups is insignificant compared to the content of carbonyl compounds. The position of the intense broad band at 1050 cm^{-1} and its shape indicate the possible formation of the intermolecular —C—O—C— and —Si—O—Si— bonds, leading to cross-linking of the polymer and a loss of the solubility of the samples oxidized at 240 °C.

The spectroscopic parameters for the nonoxidized and oxidized PTMSP films are collected in Table 2.

Note that the initial temperature of the weight loss for PTMSP in air is close to 250 °C according to the TGA

Table 2. Spectroscopic parameters* and structural units of the nonoxidized and thermally oxidized PTMSP samples

Nonoxidized sample		Oxidized samples	
ν/cm^{-1}	Assignment	ν/cm^{-1}	Assignment
—	—	3690 w	HO—(Si)
—	—	3650 w	HO—(Si)
—	—	3550 w	—OOH, free
—	—	3410 m	OH, alcohol
—	—	3380 w	—OOH, bound
2984 m	Me—(C)	2984 m	Me—(C)
2956 s	Me—(Si)	2960 m	Me—(Si)
—	—	2926	CH_2
2906 s	Me—(Si)	2906 s	Me—(Si)
—	—	2875 s	CH_2—(O)
2852 m	Me—(C)	2852 m	Me—(C)
—	—	1770	C=O, γ-lactone
—	—	1734	C=O, aldehyde
—	—	1717	C=O, ketone
—	—	1700	C=O, acid
—	—	1648	(Alk)>C=C<(Alk)
—	—	1600	C=C, in conjugation
1562 s	C=C—(Si)	1562 s	C=C—(Si)
1556 s	C=C—(Si)	1556 s	C=C—(Si)
1540 sh	C=C—(Si)	1540 sh	C=C—(Si)
1529 sh	C=C—(Si)	1529 sh	C=C—(Si)
—	—	1465	CH_2
1432 m	Me	1432 m	Me
1408 m	Me—(Si)	1408 m	Me—(Si)
—	—	1375	CH_2
1365 m	Me—(C)	1365 m	Me—(C)
1364	Me—(C)	1364 m	Me—(C)
1362 m	Me—(C)	1362 sh	Me—(C)
1360 sh	Me—(C)	1360 sh	Me—(C)
1252 s	Me—(Si)	1270	Epoxy groups
1246 s	Me—(Si)	1252 s	Si—Me_3
—	—	1246 s	Si—Me_3
—	—	1230	Epoxy groups
1180 s	Me—(C)	1180 s	Me—(C)
—	—	1124 vw	C—O, ether
—	—	1100 vw	C—O, hydroperoxide
—	—	1096 w	C—O, hydroperoxide
—	—	1088 vw	C—O, hydroperoxide
—	—	1074 w	C—O, ether
—	—	1068 vw	C—O, hydroperoxide
—	—	1060 s	C—O, alcohol
—	—	1050	C—O—C, Si—O—Si
1030 m	C—C	1030 m	C—C
1006 m	C—C	1006 m	C—C
838 vs	Si—Me_3	838 vs	Si—Me_3
758 s	Si—Me_3	758 s	Si—Me_3
748 s	Si—Me_3	748 s	Si—Me_3
686 m	Si—C	686 m	Si—C
636 m	Si—C	636 m	Si—C

* Intensities of bands: vs, s, m, w, vw, and sh are very strong, strong, medium, weak, very weak, and shoulder, respectively (are not indicated when depend on the depth of conversion).

data.[5] Our study of PTMSP by pyrolytic mass spectrometry found only tri- and tetramethylsilanes among the gaseous products of pyrolysis at 400 °C.

* * *

This study indicates the important contribution of the reaction at the C—Me group to thermal oxidation. The most interesting is the temperature region below 160 °C corresponding to the mild (in terms of conversion) oxidation step, which occurs almost completely at the C—Me group *via* the hydroxoperoxide mechanism and yields aldehyde and ether groups (presumably cyclic). These products can be formed *via* some schemes of Me group oxidation,[13] including the intramolecular recombination of macroradicals, which explains the formation of cyclic ethers[14] (Scheme 2).

Scheme 2

$$P\text{—}Me + O_2 \rightarrow P\text{—}C^{\bullet}H_2 + HO_2^{\bullet} \quad (1)$$

$$P\text{—}C^{\bullet}H_2 + O_2 \rightarrow P\text{—}CH_2\text{—}OO^{\bullet} \quad (2)$$

$$P\text{—}CH_2OO^{\bullet} \rightarrow P\text{—}CHO + {}^{\bullet}OH \quad (3)$$

$$P\text{—}C^{\bullet}H_2 + HO^{\bullet}{}_2 \rightarrow P\text{—}CH_2\text{—}OOH \quad (4)$$

$$P\text{—}CH_2\text{—}OOH \rightarrow P\text{—}CH_2O^{\bullet} + {}^{\bullet}OH \quad (5)$$

$$P\text{—}CH_2\text{—}OOH \rightarrow P\text{—}CHO + H_2O \quad (6)$$

$$P\text{—}CH_2O^{\bullet} + P\text{—}C^{\bullet}H_2 \rightarrow P\text{—}CH_2\text{—}O\text{—}CH_2\text{—}P \quad (7)$$

$$P\text{—}C^{\bullet}H_2 + {}^{\bullet}OH \rightarrow P\text{—}CH_2\text{—}OH \quad (8)$$

Cyclic ethers can be formed in reaction (8) involving two adjacent macroradicals followed by the dehydration of the resulting diols and cycle closure to dihydropyran. However, at temperatures below 180 °C, the spectra do not virtually contain bands of alcohol groups. Therefore, it seems that the most probable route for the buildup of cyclic ethers is reaction (7) of recombination of the macroradicals, which are arranged in the γ-position relatively to each other, producing the dihydropyran cycle. Most likely, the necessary condition for this reaction should be a combination of the *trans*- and *cis*-configurations in the adjacent units and the favorable orientation of the C—Me bonds. In addition, the formation of biradicals is hindered in the short spiral regions of the polymeric PTMSP chain interrupted by the segments with the nonregular conformation.[15,16] Oxidation at the Me group is the important step of the process: the resulting methylene groups are more reactive than the Me group. They are actively involved in the process and oxidized to form aldehydes with evolution of hydroxyl radicals (see Scheme 2,

reactions (2) and (3)). Thus, thermal oxidation at the C—Me group is the source of the "light" low-molecular $^{\bullet}OH$ and $^{\bullet}O_2H$ radicals, which play an important role in the high-temperature oxidation of polymers.[13]

The next vulnerable element of the PTMSP structure is the double bond, which begins to manifest its reactivity at elevated temperatures. At temperatures higher than 160—180 °C, PTMSP oxidation occurs at both the C—Me group and the double bond, combining the processes characteristic of polyolefins and unsaturated polymeric compounds. Various mechanisms of these transformations with the formation of the oxidation products, which are observed in the thermal oxidation of PTMSP (aldehydes, ketones, alcohols, γ-lactones, acids, epoxides, and ethers) were considered in several works (see, *e.g.*, Refs. 13 and 17). In addition, the mechanism of oxidation at the double bond of PTMSP and other polyacetylenes has been proposed.[5,6] The Me_3Si group is the most stable element of the PTMSP structure. Its transformations at high temperatures are mainly associated with the reactions leading to the elimination of the Me_3Si group, hydrolysis, and formation of volatile products. At the same time, the fragments of the PTMSP structure, including the $Me_3Si—C(=C)$ unit, are partially retained in the nonvolatile products of thermal oxidation at 240 °C.

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