

Oxidation of Poly(1-trimethylsilyl-1-propyne)

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SYNOPSIS

The oxidation of poly(1-trimethylsilyl-1-propyne) (PMSP) proceeded normally in air at room temperature and under mild thermal conditions. Two different bands assigned to the carbonyl groups on a side chain and on a decomposed chain end were found in the IR spectra of the oxidized PMSP membrane. However, no band assigned to a hydroxyl group was observed. An allyl-type methyl group of the PMSP was mainly autooxidized without a decrease in molecular weight at room temperature. Only the former band assigned to the carbonyl groups appeared and it had a shoulder peak. In the case of mild thermal oxidation, the decomposition started in the backbone chain and both bands appeared. When the thermal oxidation proceeded further, all bonds were broken and various carbonyl and siloxane bonds were then randomly produced. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It has been expected that the industrialization of poly(1-trimethylsilyl-1-propyne) (PMSP) as a membrane separation material is very important because it has the highest gas permeability of all polymeric membranes, e.g., the permeability coefficient for oxygen is above 10^{-7} [cm^3 (STP) cm/cm^2 s cmHg at 30°C]. Several studies concerning PMSP have been reported.¹⁻¹⁰ However, PMSP membranes have the following problems¹⁻¹⁰: (i) The separation factor is low, e.g., the ideal separation factor for oxygen/nitrogen is below 2.0; (ii) hysteresis of the permeability; and (iii) thermal treatment instability.

An extensive study has been in progress for several years in our laboratory concerning the modification and permeability of PMSP in order to solve these problems.^{3,4,6,8} In this article, the oxidation behavior of the PMSP, corresponding to problems (ii) and (iii), was investigated in detail using FTIR, UV visible, and DSC analyses.

Nonsubstituted polyacetylene $[(\text{CH})_x]$ is well known to be easily oxidized not only under thermal conditions but also at room temperature.¹¹⁻¹⁴ The oxidation behavior is different from the *cis-trans*

conformation of $(\text{CH})_x$ depending on the polymerization catalysts and thermal isomerization. Unpaired electrons were found in $(\text{CH})_x$ using electron spin resonance spectroscopy (ESR). The spin density of amorphous $(\text{CH})_x$ changed irreversibly from 10^{18} to 10^{17} (spins/g) after exposing the $(\text{CH})_x$ to oxygen. Furthermore, the oxygen atom was identified in the exposed sample using elemental analysis.¹¹ The oxidation mechanism of $(\text{CH})_x$ is based on the possibility that a hydroperoxide group was formed and caused decomposition; hydroxyl and carbonyl groups were then produced.¹² However, a substituted polyacetylene, which is expected to show the same behavior as that of $(\text{CH})_x$ based on the substituent effect, does not always occur.

In the case of a substituted polyacetylene, few articles were reported before Ref. 15 was published. A study of the thermal decomposition, which in most cases depended on oxidation, was undertaken to produce several mono- and disubstituted polyacetylenes. The substituents were alkyl-, phenyl-, chlorine-, and silicone-containing groups. Most polymers easily decomposed, which was determined by their molecular weight decrease. It was assumed that the decomposition occurred at the carbon-carbon double bonds in the backbone chain and the hydroxy and carbonyl groups appeared at the end of each decomposed chain. This result was similar to the case of $(\text{CH})_x$. However, none of the polymers from *tert*-butylacetylene, the silicone disubstituted acetylenes,

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e.g., PMSP, and aromatic disubstituted acetylenes were oxidized or showed any molecular weight decrease in air at room temperature for 3 months.¹⁵ Another group has reported a different result, in which PMSP stored for about 4 years under ambient conditions was oxidized.¹⁶

The spin densities of the substituted polyacetylenes were below 10^{15} (spins/g).¹⁷ This result showed that free radicals were too unstable to be formed and to continue to exist. The backbone chains of these polymers were twisted because of the substituents.¹⁷ The thermal formation of biradicals on the backbone was then considered as the initiation of the thermal decomposition mechanism.¹⁵

EXPERIMENTAL

Materials

PMSP was synthesized according to Masuda's method.¹⁸ The polymerization was carried out under dry nitrogen using TaCl_5 as a catalyst in toluene at 80°C for 24 h; [1-trimethylsilyl-1-propyne] = $0.5M$ and $[\text{TaCl}_5]$ = $0.02M$. The obtained polymer was isolated by precipitation from a large amount of methanol, filtered, and dried under vacuum. The polymer yield was 85%. The weight- (M_w) and number-average (M_n) molecular weights of the product were 700,000 and 310,000, respectively. The polydispersity ratio (M_w/M_n) was 2.3. These values were determined using gel permeation chromatography. The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) and found to be above 350°C . The IR spectrum of the synthesized PMSP membrane is shown in Figure 1. The PMSP membranes having various thicknesses were prepared by the casting method. The synthesized PMSP was dissolved and then cast from a toluene solution onto a glass plate and dried under vacuum. All membranes were immersed in methanol to keep the membranes fresh. In most cases, a thin membrane with a thickness of below $10\ \mu\text{m}$ was used. A thick membrane with about $200\ \mu\text{m}$ thickness was used for the thermal treatment.

Analyses

The FTIR spectra were recorded on an FTIR Perkin-Elmer 1800 by the transmission and total internal reflection (ATR) methods at a resolution of 4 and $2\ \text{cm}^{-1}$. The samples for the former method were prepared as a thin film or a KBr plate. A KRS-5 crystal was used and the incident angle to the crystal was 45° using the ATR method. UV-visible

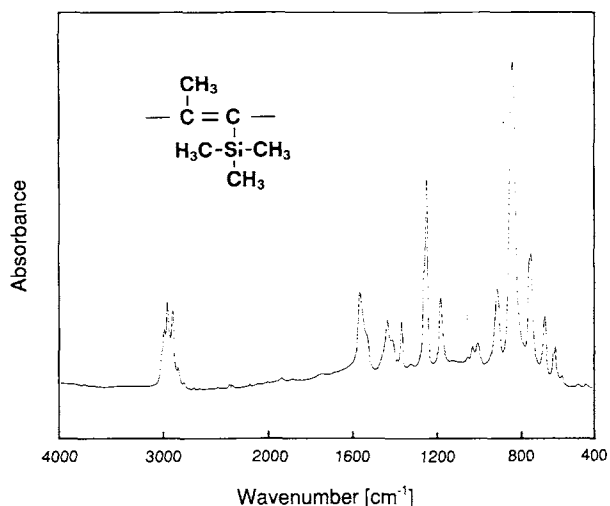


Figure 1 IR spectrum of the fresh PMSP membrane.

absorption spectra were obtained at 25°C in cyclohexane using a Hitachi Model 200-20. DSC was determined using a Perkin-Elmer DSC 7 at a heating rate of $20^\circ\text{C}/\text{min}$. ESCA measurements were carried out using a JEOL XPS JPS-80; $\text{MgK}\alpha$ radiation; $\theta = 90^\circ$. Gel permeation chromatography was done using a Tohso HLC-8020. M_w and M_n were determined on the basis of a polystyrene calibration. Intrinsic viscosities ($[\eta]$) were measured in toluene at 30°C .

RESULTS AND DISCUSSION

Characterization of the Synthesized PMSP

The characterization of the synthesized PMSP is shown in Table I. The data of Samples 2–5, which were synthesized according to Refs. 17 and 18, are listed for comparison with Sample 1. Samples 2 and 5 are the PMSPs that showed no oxidation and oxidation at room temperature in Refs. 15 and 16, respectively. There is no information about the characterization except for the molecular weight. Other PMSPs are listed in the same table. The viscosity of Sample 1 was smaller than that of the others, and the λ_{max} and ϵ_{max} values were different when the same catalyst and solvent were used. The λ_{max} value of Sample 1 was smaller than that of Samples 3, 4, and 19. It is well known that the λ_{max} value shifts to the longer wavelength side, and the ϵ_{max} value increases when the number of double bonds in a molecule increases.^{18,20,21}

The λ_{max} value of Sample 1 was similar to that of 1,3-butadiene having two carbon-carbon double bonds in the molecule: $\lambda_{\text{max}} = 217\ \text{nm}$ and ϵ_{max}

Table I Characterization of Poly(1-trimethylsilyl-1-propyne)

No.	\bar{M}_w ($\times 10^4$)	\bar{M}_w/\bar{M}_n	λ max (nm)	ϵ max ($M^{-1} \text{ cm}^{-1}$)	$[\eta]$ (dL/g)	Ref.
1	70	2.3	220.8	5460	1.6	This work
2	138	3.0	— ^a	— ^a	— ^a	[15]
3	130	2.2	235	3400	— ^a	[19]
4	73	5.6	273	120	5.4	[17, 18]
5	59	4.7	— ^a	— ^a	4.2	[16]

^a No information.

= $20,900 \text{ M}^{-1} \text{ cm}^{-1}$.²² This indicated that Sample 1 was more difficult to conjugate with many carbon-carbon double bonds in comparison with Samples 3 and 4 and that these conformations were different from each other.

Oxidation at Room Temperature

The ESCA spectrum of the PMSP membrane stored in air at room temperature for 6 months is shown in Figure 2. The room temperature had been controlled between 20 and 25°C. The existence of oxygen in the PMSP exposed to air was identified. The oxygen content was estimated at 6.6%. For the purpose of analyzing what groups were produced by the oxidation, FTIR and ¹H- and ¹³C-NMR measurements were carried out. The IR spectra showed important information. However, in the NMR spectra of the oxidized PMSP samples, the peak intensity was not larger than the noise intensity; therefore, the NMR measurement did not give any clear data. We have continued the NMR analysis.

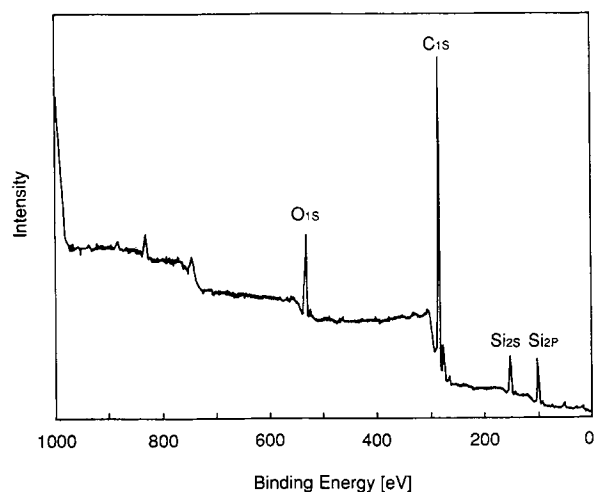


Figure 2 ESCA spectrum of the PMSP membrane stored in air at room temperature for 6 months.

Figure 3 shows the IR spectra of the fresh PMSP membrane (A) and the PMSP membrane stored in air at room temperature for 9 months (B, the stored A membrane) and their difference spectrum (C). The absorbance values of all spectra in this work were less than 1. The band at 1246 cm^{-1} was used as a reference. This band is due to the CH_3 symmetric deformation of the $\text{Si}(\text{CH}_3)_3$ group. The thickness of the measured sample was below $10 \mu\text{m}$, which was measured using the transmission method.

In the case of the substituted polyacetylenes having several alkyl groups, i.e., poly(2-octyne) and poly(1-hexyne), they were decomposed and the molecular weight decreased in air at room temperature after 3 months. The bands due to the carbonyl group stretching vibration ($\text{C}=\text{O}$) and hydroxy group stretching vibration (OH) were then observed in the IR spectra. However, PMSP was not oxidized and showed no molecular decrease.¹⁵

Another research group reported that the PMSP was oxidized under ambient conditions because the

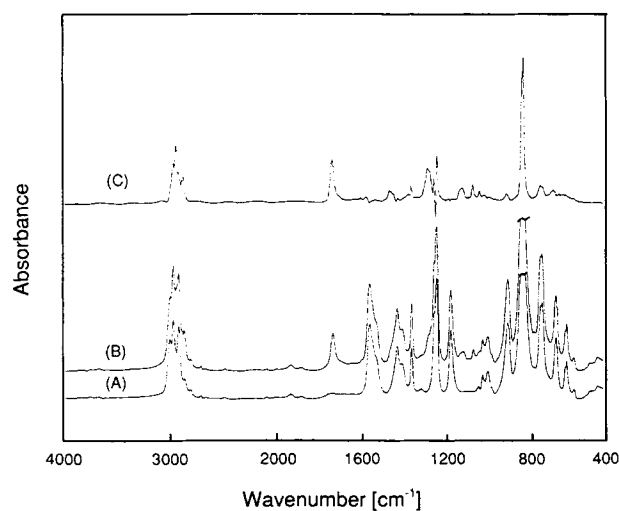


Figure 3 IR spectra of the (A) fresh PMSP membrane, (B) PMSP membrane stored in air at room temperature, and (C) difference spectrum [(B) - (A)].

band at 1740 cm^{-1} in the IR spectrum and the signal between 120 and 130 ppm in the ^{13}C -NMR spectrum appeared after storage for about 4 years.¹⁶

The bands near 1730 , 1280 , and 850 cm^{-1} and some bands between 3000 and 2900 cm^{-1} appeared after storage in air at room temperature in Figure 3. These bands are due to the $\text{C}=\text{O}$ stretching, carbon-carbon stretching ($\text{C}-\text{C}$), and carbon-hydrogen stretching ($\text{C}-\text{H}$), respectively. The band at 1736 cm^{-1} has a shoulder peak around 1700 cm^{-1} . It seems that the $\text{C}=\text{O}$ groups are partially conjugated with the $\text{C}=\text{C}$ bonds in the backbone chain: $-\text{C}=\text{C}-\text{CO}(\text{R})$. The region from 4000 to 3200 cm^{-1} is associated with $\text{O}-\text{H}$ stretching. No band was observed in this region in Figure 3(B). The M_w , M_n , and viscosity of the fresh PMSP and that stored in air at room temperature for 9 months had the same values. This means that the decomposition did not occur. However, the oxidation occurred because of the presence of the 1736 cm^{-1} band in the IR spectra and the O_{1s} core level in the ESCA spectra. Yampol'skii et al. reported that the oxidation at room temperature occurred at the $\text{C}=\text{C}$ bond and some $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ groups were produced on the backbone chain.¹⁶ The phenomena were analyzed in more detail.

Quantitative infrared analysis was performed by measuring the absorbance at the absorption maximum of the analytical band in Figure 3 and analyzing the results using the peak height method. Figure 4 shows the dependence of the A_{1736}/A_{1246} and A_{1561}/A_{1246} ratios on total time in air at room temperature in the IR spectra of the PMSP membrane. These wavenumbers at 1736 , 1561 , and 1246 cm^{-1} are due to the band assigned to the $\text{C}=\text{O}$ stretching, the carbon-carbon double bond olefinic stretching ($\text{C}=\text{C}$), and the CH_3 symmetric deformation of the $\text{Si}(\text{CH}_3)_3$ group, respectively. The symbols of A_{1736} , A_{1561} , and A_{1246} mean the true absorbance at 1736 , 1561 , and 1246 cm^{-1} , respectively. The band at 1246 cm^{-1} was used as a reference. The ordinate represents the A_{1736}/A_{1246} and A_{1561}/A_{1246} at the measurement time over that of the first point. The first point of the A_{1561}/A_{1246} is 0 day, but that of the A_{1736}/A_{1246} was used at 10 days for convenience because no band at 1736 cm^{-1} was observed at 0 day. The absorbance ratio of the first point was 100%. The A_{1736}/A_{1246} ratio increased with time; however, the A_{1561}/A_{1246} ratio was almost constant.

We reported that an endothermic peak appeared around 50°C in the DSC curve of the brominated PMSP, because the bromination occurred at the $\text{C}=\text{C}$ bond, and the $-\text{CBr}-\text{CBr}-$ bond was produced as a result of the IR and UV-visible anal-

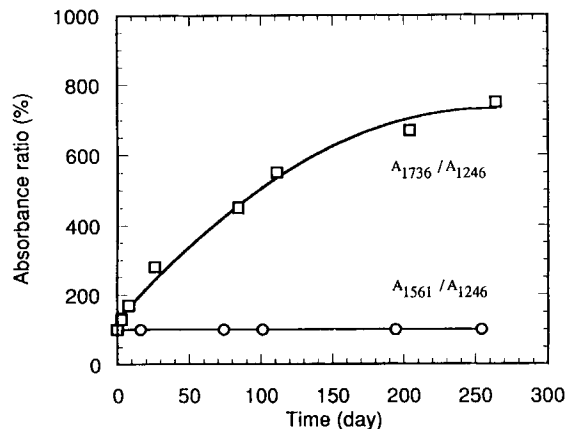


Figure 4 Dependence on total time in air at room temperature of the (\square) A_{1736}/A_{1246} and (\circ) A_{1561}/A_{1246} ratios in the IR spectra of the PMSP membrane.

yses.²³ Even if the bromine content was only 3 wt %, the peak was clearly observed. Most polymers show an endothermic peak, which means the glass transition point (T_g), between -130 and 300°C in their DSC curves.²⁴ No peaks were observed between -160 and 350°C in the DSC curves of the fresh PMSP and the PMSP stored in air for 1, 3, and 6 months and 6 years.

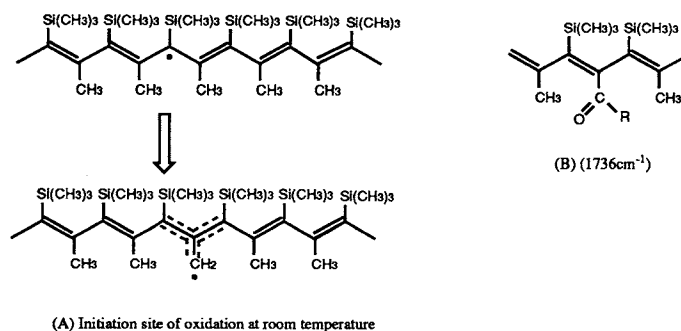
These results mean that the $\text{C}=\text{O}$ group was mainly produced without a reaction at the carbon-carbon double bond in the PMSP backbone chain. Therefore, it is suggested that the allyl-type CH_3 group [$-(\text{CH}_2)\text{C}=\text{CR}-$, $\text{R}:\text{Si}(\text{CH}_3)_3$] was oxidized and changed to a carbonyl group. The product has a mixed structure of some groups having $\text{C}=\text{O}$ groups [see Fig. 5(B)].

Table II shows the dependence of the absorptivity ratio on total time in air at room temperature at the λ max value in the UV visible spectra of the PMSP membrane. The λ max value was maintained and the absorptivity ratio increased with time. This result was caused by the $\text{C}=\text{O}$ group.

The initiation of the oxidation is presumed to occur as follows: The spin density of PMSP is below 10^{15} (spins/g).¹⁷ However, this suggests that some unpaired electrons exist on the backbone chain and they are transferred to an allyl-type CH_3 group and become the initiation site of the oxidation [see Fig. 5(A)]. Although some unpaired electrons also seem to exist at the $\text{C}=\text{C}$ bonds in the backbone chain, little oxidation occurs at this site. It is assumed that these results were due to the effects of steric hindrance of the large $\text{Si}(\text{CH}_3)_3$ group and insufficient energy for reaction at room temperature.

The different phenomena related to the oxidation at room temperature of the PMSP synthesized by

Oxidation at room temperature



Thermal oxidation

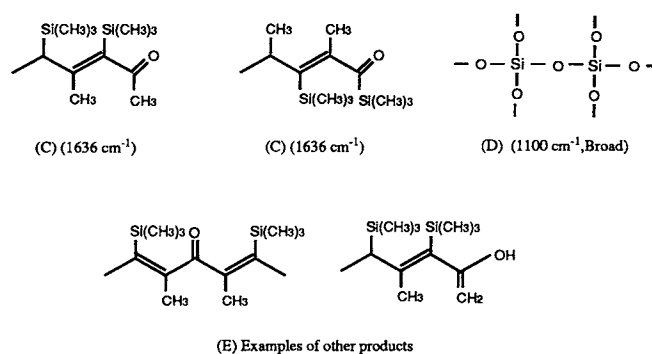


Figure 5 Summary of the oxidation products.

each research group were observed in Refs. 15 and 16 and in this work. This resulted in a difference in the conformation and configuration of each PMSP.

Thermal Oxidation

The IR spectra of the PMSP membrane stored in air at 150°C are shown in Figure 6. The heated sample, which had a thickness below 10 μm, was interposed between KBr plates. This technique was used because the heated sample membrane was brittle. The absorbance of the sample treated for 4 h [Fig.

6(D)] was smaller than that of the others; therefore, the absorbance scale of only this sample was magnified the same scale as that of the others.

After treating the material for 30 min, the bands assigned to the Si(CH₃)₃, C=C, and CH₃ groups were weaker and the band assigned to the C=O group was stronger. There were several bands between 1800 and 1500 cm⁻¹; therefore, various C=O groups would be produced. One hour later, the main bands were then attributed to the C=O group and the siloxane group (Si—O—Si). Finally, 4 h later, the main structure changed to that of the Si—O—Si group [see Fig. 5(D)]. The heating energy at 150°C is thought to be sufficient to break all bonds of the PMSP, i.e., carbon-hydrogen (C—H), carbon-carbon (C—C), carbon-carbon double bond (C=C), and carbon-silicon (C—Si) bonds, and produce a siloxane bond (Si—O—Si) that is stable under heating.²⁵ No band was observed in the region from 4000 to 3200 cm⁻¹ characteristic of OH stretching. In this case, the OH or Si—O—R groups appeared to change to the C=O group, which was a more stable structure than that of the OH group.

Table II UV Visible Spectra Data of the PMSP Stored in Air at Room Temperature

Time (Day)	λ max (nm)	ε max (M ⁻¹ cm ⁻¹)
0	220.8	5460
127	220.8	5470
146	220.8	6120
211	220.8	6690

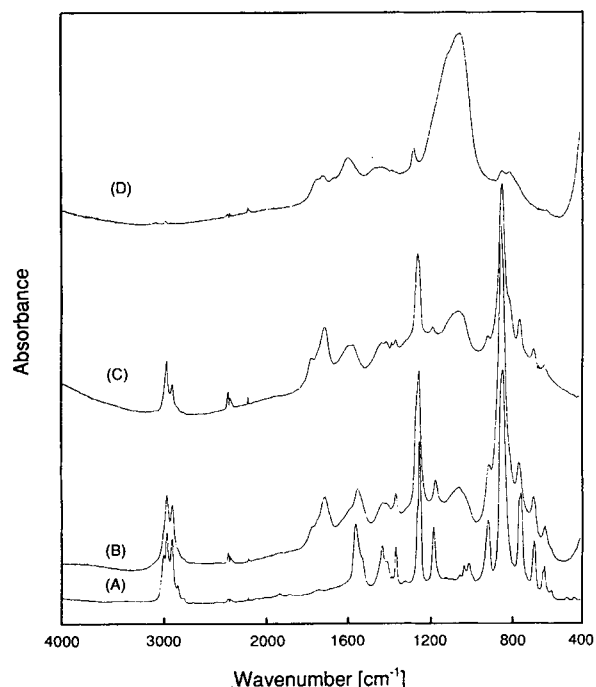


Figure 6 IR spectra of the (A) fresh PMSP membrane, PMSP membranes stored in air at 150°C for (B) 30 min, (C) 1 h, and (D) 4 h.

Figure 7 shows the DSC curves of the PMSP stored in air at room temperature and 150°C. The fresh PMSP had no peak between -160 and 350°C. The PMSP stored at room temperature for 6 years also had no peak but showed a curve. In the thermal case at 150°C, an exothermic peak around -120°C, related to some transitions of the siloxane group produced during the oxidation, appeared and showed a change toward the exothermic side above 200°C. However, after heating for 4 h, the peak was not found because the main structure changed to that of the Si—O—Si group similar to the silica structure; the degree of change toward the exothermic side then increased. This means that the heat stability of the oxidized PMSP was reduced as oxidation proceeded. The silica powder (Aerosil), which has Si—OH groups on the surface, had an endothermic peak around 0°C associated with absorbed water. This result means that the Si—OH group was not produced, nor did it exist stably in the oxidized PMSP.

For a more detailed analysis, the thermal oxidation was carried under milder conditions. Air was substituted with nitrogen gas in order to reduce the oxygen concentration, and the temperature was 120°C. The sample thickness was about 200 μm , and the FTIR measurement was carried out using the ATR method. The surface measurement depth using

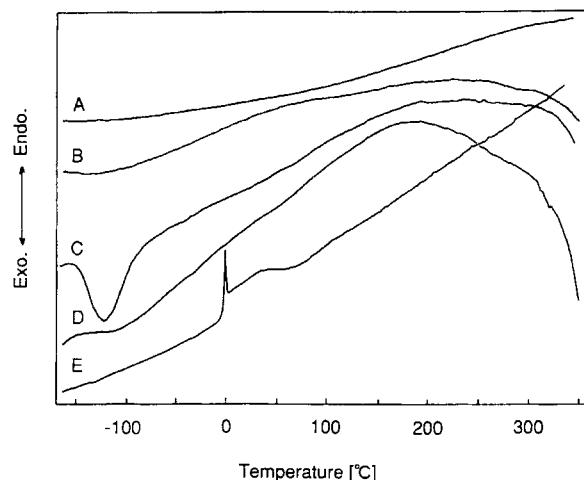


Figure 7 DSC curves of (A) the fresh PMSP, (B) the PMSP stored in air for 6 years, the PMSP stored in air at 150°C for (C) 1 h and (D) 4 h and (E) silica powder (Aerosil).

a KRS-5 crystal with an incident angle of 45° was 1–2 μm .

Figure 8 shows the FTIR-ATR spectra of the PMSP membrane treated at 120°C in nitrogen, compared with the PMSP membrane stored in air for 1 month. The region is between 1800 and 1600 cm^{-1} . Two bands assigned to the C=O group at 1734 and 1636 cm^{-1} were observed in the heated

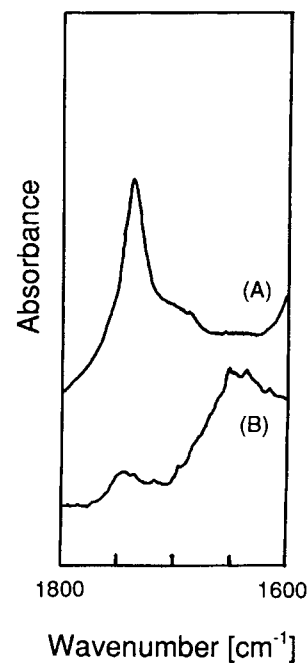


Figure 8 FTIR ATR spectra of the PMSP membranes (A) stored in air for 1 month and (B) treated at 120°C in nitrogen for 1 h.

PMSP membrane. In comparison with the case at room temperature, a different C=O group at 1636 cm^{-1} appeared. It was presumed that the difference in the two C=O groups [the one at 1734 cm^{-1} was of the same state at room temperature and that at 1636 cm^{-1} had a conjugated structure ($-\text{C}=\text{C}-\text{C}=\text{O}$)] was then shifted by about 100 cm^{-1} . In the case at room temperature, the band shifted by about 30 cm^{-1} from 1736 to near 1700 cm^{-1} . The band near 1700 cm^{-1} is due to the C=O group on a side chain as the result of the oxidation at room temperature. This means that conjugation of the group near 1700 cm^{-1} was inhibited more than that at 1636 cm^{-1} .

Table III shows the results of the quantitative analysis of the UV-visible spectra, the viscosities, and FTIR-ATR spectra. When using the ATR method in multiple samples, it is difficult if not impossible to duplicate the pressure and contact between sample and crystal. The ATR method does not result in a linear plot of signal vs. concentration. Therefore, an absolute comparison between samples was difficult using the ATR method. However, a relative comparison between bands in the same spectrum would be possible. The samples at mild treatment (Samples 2–5) were analyzed using the ATR method. However, the FTIR-ATR measurement of Samples 6–8 did not give any clear spectra or did not carry out quantitative analysis because the samples were warped or a heavy change in the spectra on oxidized samples was observed. After heating, the viscosity had decreased. Decomposition seems to have occurred at the C=C bonds. The A_{1636} values were stronger than were the A_{1734} values at mild treatment. The ϵ max values increased after the heat treatment. The λ max values shifted about 1 nm

above 150°C . These results from the UV-visible analysis mean that the C=O concentration above 150°C was higher than that below 150°C ; i.e., room temperature and 120°C . The effect of the C=O group was then observed in the UV-visible spectra. These results indicate that the C=C bond is easily broken in comparison with the side-chain substituent.

The decomposition mechanism was reported,^{15,17} i.e., the substituted polyacetylene was decomposed during the heat treatment and a C=O group was produced on the decomposed chain end: $-\text{CR}=\text{CR}-\text{CO}(\text{R})$. In the case of mild treatment at 120°C in nitrogen, the main band at 1636 cm^{-1} appears to be due to the conjugated C=O group on the decomposed chain end [see Fig. 5(C)]. In comparison with the conjugated C=O group on a side chain, the conjugation of this group was not inhibited by a steric effect. Therefore, a large shift of about 100 cm^{-1} occurred. When the thermal oxidation proceeded, all bonds were broken and various C=O groups were randomly produced as shown in Figure 6.

CONCLUSIONS

The following conclusions can be drawn from the results of this study:

1. The oxidation of poly(1-trimethylsilyl-1-propyne) (PMSP) proceeded normally in air at room temperature and under mild thermal conditions. Two different bands assigned to the carbonyl groups were found in the IR spectra of the oxidized PMSP membrane.

Table III Characterization of the Heat-treated PMSP Membranes

No.	Condition			FTIR Spectrum $A_{1734} : A_{1636}$	UV Visible Spectrum		Viscosity [η] (dL/g)
	Ambience	Temp ($^\circ\text{C}$)	Time (h)		λ max (nm)	ϵ max ($M^{-1}\text{ cm}^{-1}$)	
1	Blank	—	—	—	220.8	5460	1.55
2	Vac.	120	24	36 : 64	220.8	6290	1.52
3	Vac.	120	120	28 : 72	220.8	8610	1.18
4	N_2	120	1	27 : 73	220.8	6500	1.40
5	N_2	150	1	22 : 78	220.0–220.8	7650	1.21
6	N_2	150	24	— ^a	218.8–220.6	5700	0.13
7	N_2	200	1	— ^a	220.0–220.8	6740	1.16
8	Air	150	1	— ^a	219.6–220.6	9750	1.06

^a The values could not be determined.

However, no band assigned to a hydroxyl group was observed.

2. The synthesized PMSP was easily autooxidized in air at room temperature. An allyl-type CH_3 group on the side chain was oxidized without a molecular weight decrease.
3. It was presumed that the presence of unpaired electrons in the slightly conjugated $\text{C}=\text{C}$ bonds acts as the active site of the initiation. Some of the unpaired electrons are transferred to the allyl-type CH_3 group and become the initiation sites of oxidation at room temperature.
4. In the case of thermal oxidation, decomposition first started at the $\text{C}=\text{C}$ bonds and several $\text{C}=\text{O}$ groups were produced on the side chains and decomposed chain ends. When the oxidation was continued, all bonds were broken and various $\text{C}=\text{O}$ and $\text{Si}-\text{O}-\text{Si}$ bonds were then randomly produced.
5. The $\text{C}=\text{O}$ groups, which conjugated at the $\text{C}=\text{C}$ bond in the backbone chain, on a side chain and a decomposed chain end appeared at different bands in the IR spectra at room temperature and under mild thermal conditions. In comparison with the $\text{C}=\text{O}$ group on a decomposed chain end, the conjugation of that on a side chain was inhibited by a steric effect.

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