

# Fourier Transform Infrared Spectroscopy Study of Poly(1-trimethylsilyl-1-propyne) Aging

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**ABSTRACT:** The influence of various factors on the aging of poly(1-trimethylsilyl-1-propyne) (PTMSP) during long-term storage in air was investigated with Fourier transform infrared spectroscopy. Most attention was paid to the differentiation of oxidation, the reduction of the free volume, and the absorption of low-molecular-weight compounds from the environment. IR spectra of PTMSP samples stored from 1–2 months to 6.5 years revealed C=O, C–O, and C–H bands that had been earlier attributed to polymer oxidation products. It was established, however, that these bands completely disappeared from IR spectra of the aged samples after their soaking in ethanol. Spectra of dried residues of ethanol extracts displayed all these bands and did not show any bands of polymer chain frag-

ments. Gas chromatography/mass spectrometry analysis proved that the residues were composed mainly of various dialkyl phthalates. Special experiments showed that PTMSP films easily absorbed di-*n*-butyl phthalate vapors. IR spectra of the films stored for a long time showed no decrease in double-bond and methyl group bands. It was concluded that the polymer did not undergo oxidation in air at room temperature for at least 6.5 years. The absorption of plasticizer vapors (and possibly other compounds) from the environment and the reduction of the free volume were the main reasons found for PTMSP aging. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2523–2527, 2007

**Key words:** aging; FTIR; polyacetylenes

## INTRODUCTION

Poly(1-trimethylsilyl-1-propyne) (PTMSP), a glassy (glass-transition temperature  $> 250^{\circ}\text{C}$ ), rigid-chain polymer having a large nonequilibrium free volume (20–34%), possesses extremely high gas permeability.<sup>1–3</sup> This property of PTMSP makes possible its application as a membrane material. However, the high permeability of PTMSP can be lost during its storage under ambient conditions. This process is usually considered the aging of the polymer. It is thought that three factors may be responsible for the polymer property changes: chemical aging (oxidation in air), physical aging (free-volume reduction due to relaxation), and sorption of low-molecular-weight compounds from the environment.<sup>2</sup> For example, the last factor has been suggested to explain the significant reduction of the gas permeability of PTMSP films stored *in vacuo*.<sup>4</sup> The effect was believed to be due to the sorption of hydrocarbons from vacuum pump oil. It has also been noted that compressor and vacuum pump oil and additives in gasket plastics in permeability apparatus can increase the weight of PTMSP up to 20%.<sup>5,6</sup>

In a number of works, the presence of bands of carbonyl groups in IR spectra of PTMSP films stored in air at room temperature for different periods (30 days,<sup>3</sup> 9 months,<sup>2,7</sup> and 2–8 years<sup>8</sup>) has been interpreted as a result of polymer oxidation. At the same time, an IR spectrum of a PTMSP sample stored in the dark at room temperature for 3 months showed no bands characteristic of oxidation products.<sup>9</sup>

The contradictions of the results could be due to the aforementioned factors, which simultaneously affect PTMSP aging. In addition, systematic studies of the structural changes and sorption of low-molecular-weight compounds during the storage of the polymer in a single experiment have never been reported. This study was undertaken to apply Fourier transform infrared (FTIR) spectroscopy to the estimation of the contributions of various factors to PTMSP aging during long-term storage at room temperature.

## EXPERIMENTAL

### Material and sample preparation

A PTMSP sample with a random distribution of *cis* and *trans* units (60 : 40) was prepared with  $\text{NbCl}_5$  as the catalyst<sup>1</sup> and purified as described earlier.<sup>10</sup>

The polymer had the following characteristics: a glass-transition temperature greater than  $200^{\circ}\text{C}$ , an intrinsic viscosity of 0.42, a weight-average molecular weight of  $25 \times 10^4$ , and a weight-average molecular

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weight/number-average molecular weight ratio of 1.56. PTMSP films 10–40  $\mu\text{m}$  thick were prepared via casting from toluene solutions (concentration = 0.5%) on the glass plate. The films were removed from the support and dried in air over 3 days. The absorbance of bands in IR spectra was used for the estimation of the PTMSP film thickness. To do this, a calibration curve was used. The band intensities for the films with a thickness greater than 30  $\mu\text{m}$  were measured, and this was followed by extrapolation to the zero thickness.

The films were stored in a glass jar under a glass cover at room temperature (19–25°C) in a writing-table box, and the IR spectra were recorded during 24 months at regular intervals.

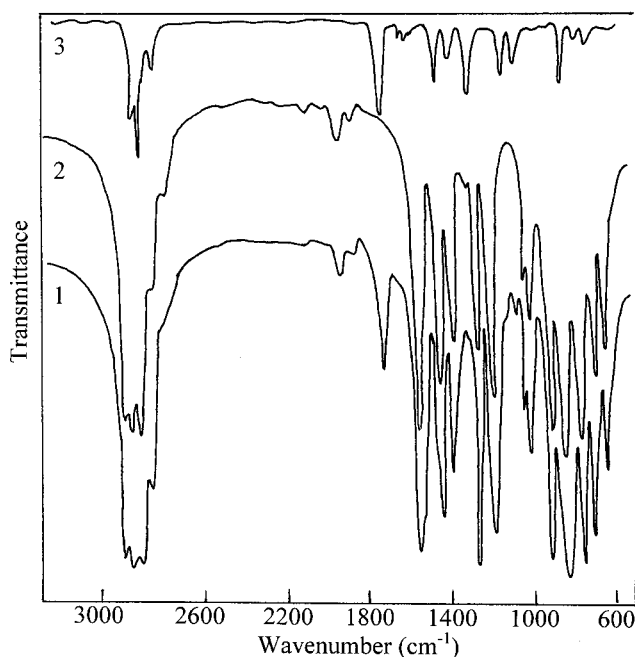
### Instrumentation

FTIR spectra were recorded in the 4000–400- $\text{cm}^{-1}$  frequency range with an AF-1 FTIR spectrometer (NTTs UP RAS) designed at the Research and Engineering Center of Unique Instrumentation of the Russian Academy of Sciences (Moscow, Russia; the maximum resolution was 1  $\text{cm}^{-1}$ , and the accuracy in the determination of the wave numbers was 0.1  $\text{cm}^{-1}$ ). The relative intensities of the bands were defined as the ratio of the analytical band absorbance to that of the band at 636 in the spectrum of PTMSP. The band was due to the  $\nu_s(\text{Si}-\text{C}_3)$  vibration in the trimethylsilyl group, which was the most stable moiety of the polymer structure. The values of the absorbance were determined from the maxima of the absorption bands.

Gas chromatography/mass spectrometry (GC/MS) analysis was performed with a Finnigan MAT 95 XL gas chromatograph/mass spectrometer (Bremen, Germany) [in the chromatographic part, a capillary column (30 m long, 0.19-mm i.d.) containing a polydimethylsiloxane stationary phase was used; the thermostat was heated from 20 to 290°C at a speed of 10°/min].

## RESULTS AND DISCUSSION

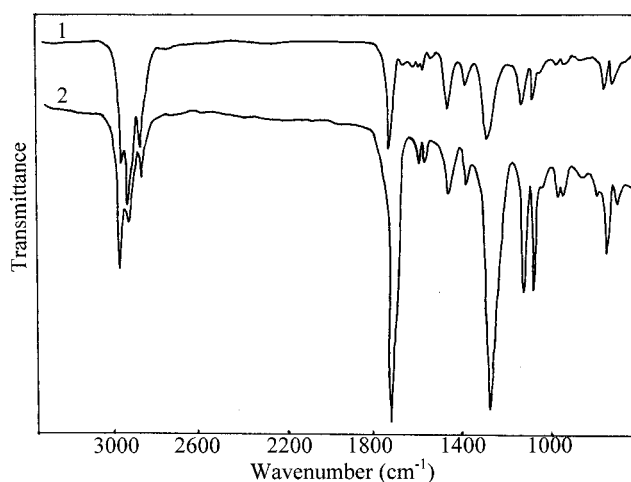
The IR spectra of the freshly prepared PTMSP film and the same film stored in air for 2 years are given in Figure 1. The spectrum obtained by the subtraction of the fresh sample spectrum from that of the aged sample is also given. The time-dependent changes for the 10- $\mu\text{m}$ -thick film of the PTMSP spectrum are shown in Figure 1 as a typical example. The character of the spectral changes is mainly the same as that for the films 30 or 40  $\mu\text{m}$  thick. The bands of the hydroxyl groups are missing from the spectra of the aged samples, as are those of the Si—O—Si bonds. Figure 1 shows that the most intense new bands are near 1740–1713, 1000–1280, and 2800–2950  $\text{cm}^{-1}$ ; these bands are due to the C=O, C—O, and C—H



**Figure 1** IR spectra of a PTMSP film (1) after and (2) before storage for 2 years and (3) the difference spectrum (spectrum 1 – spectrum 2).

bonds (in  $\text{CH}_2$  and  $\text{CH}_3$  groups), respectively. The latter bands may be attributed to the products of polymer oxidation and/or low-molecular-weight compounds sorbed by the polymer from air. To differentiate these factors, the aged PTMSP films were soaked in ethanol (a nonpolymer solvent) at room temperature to extract possible low-molecular-weight compounds. The IR spectra of the residues (after the evaporation of ethanol from the extract) and of the dried films were recorded. The IR spectrum of the PTMSP film after soaking was identical to that of a freshly prepared polymer. Neither trimethylsilyl group bands nor bands of any other polymer fragments were observed in the spectra of the extraction products. The IR spectrum of the dry residue of the ethanol extract was consistent with that of a mixture of dialkyl phthalates, namely, di-*n*-butyl and dioctyl phthalates. For illustration, the IR spectrum of the dried residue of the ethanol extract is presented in Figure 2 along with that of di-*n*-butyl phthalate (DBP). These results were confirmed by GC/MS analysis.

The obtained results indicate that aged PTMSP does not contain any oxidized fragments chemically bounded to the polymer molecule. All new bands in the spectrum of the aged polymer are due to absorbed impurities, mainly dialkyl phthalates. The esters of phthalic acid are known to be widely distributed polymer plasticizers whose content in commercial polymer materials can vary from 1 to 2 to 100% of the polymer mass. In the course of time,



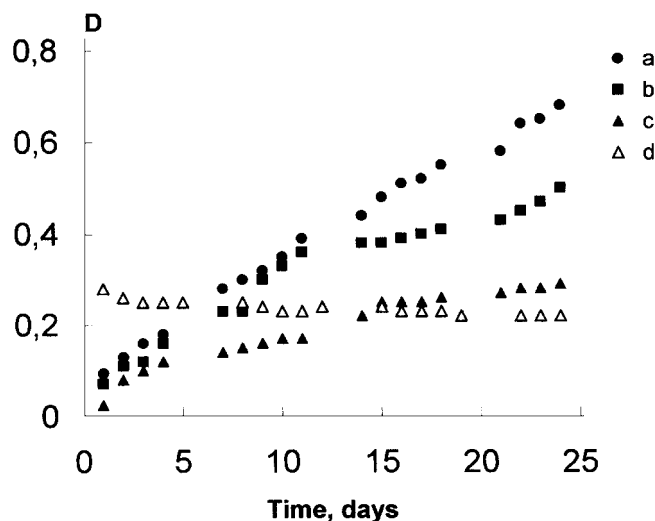
**Figure 2** IR spectra of dried residues of ethanol extracts of (1) PTMSP and (2) DBP.

plasticizers migrate out of the bulk of the polymer to its surface,<sup>11</sup> leave it, and pollute the environment.<sup>12</sup> For example, an analysis of air performed with GC/MS has indicated that the amounts of DBP in the air of office compartments and of pure compartments for semiconductor production are 350–780 and 100 ng/m<sup>3</sup>, respectively.<sup>13</sup> According to our data, the source of dialkyl phthalates sorbed by PTMSP samples from air may be the polymeric coatings of floor and laboratory tables, book jackets, cable insulation, and so forth.

A simulation of the accelerated sorption of plasticizer vapors by PTMSP films was performed with DBP, one of the most commonly used plasticizers. PTMSP films 10, 30, and 40  $\mu\text{m}$  thick were placed for 25 days at room temperature in a glass vessel in such a manner that the distance between the films and DBP surface did not exceed 2 cm and free access of the DBP vapors to both sides of the films was provided. Figure 3 demonstrates the intensity of the carbonyl group band at 1730  $\text{cm}^{-1}$  in the spectra of PTMSP versus the time of exposure of films to the DBP vapors. The dependence of the DBP content on the PTMSP film thickness provides evidence of the diffusion character of the process. It was established that the weight of the films 10–40  $\mu\text{m}$  thick increased by 13–19 wt %.

The rate of desorption of DBP from a PTMSP film was studied as well. The film 40  $\mu\text{m}$  thick, containing DBP, was kept in air far from possible sources of plasticizer vapors at room temperature for 25 days. Figure 3 indicates that the desorption of DBP from the PTMSP film occurred only slightly during the first 5 days, and further changes were insignificant.

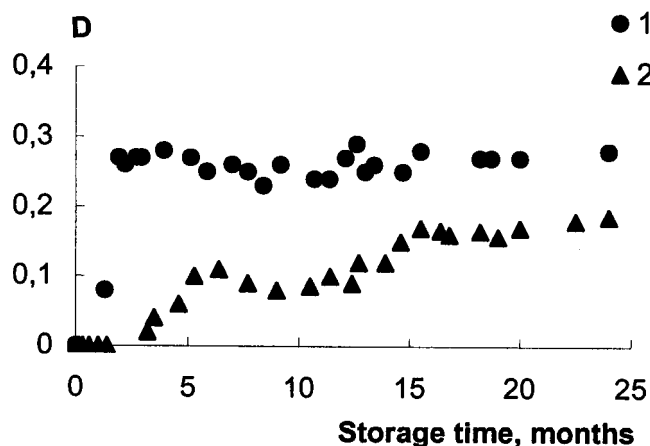
Returning to the absorption of phthalate vapors during long-term storage in air in closed compartments, we refer to Figure 4, which presents the dynamics of plasticizer absorption by PTMSP films



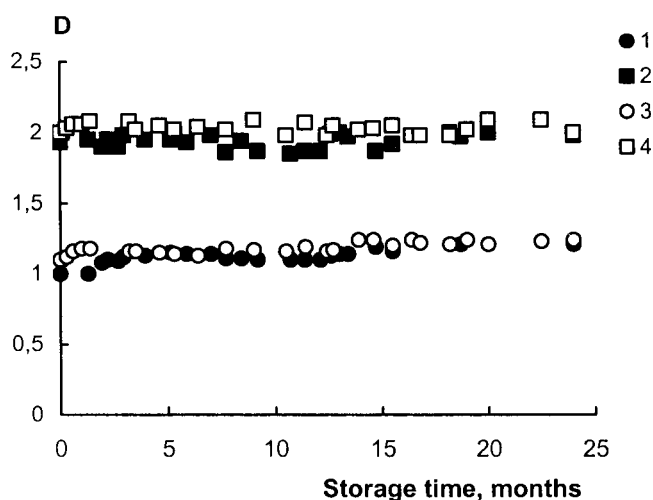
**Figure 3** Carbonyl band (at 1730  $\text{cm}^{-1}$ ) intensity ( $D$ ) in the IR spectra of (a–c) PTMSP films versus the time of their exposure to DBP vapors and (d) a PTMSP film containing absorbed DBP versus the time of its storage in air. The film thicknesses were (a) 10, (b) 30, and (c,d) 40  $\mu\text{m}$ .

as the intensity of the carbonyl bands versus the time of storage. The sorption of phthalates by PTMSP films proceeds most intensely during the initial 5 months of their storage. The carbonyl group bands of phthalates arise in the spectrum of freshly prepared films stored in air for 20–30 days.

Figure 5 demonstrates the intensity of the bands attributed to C=C (1548  $\text{cm}^{-1}$ ) and C—CH<sub>3</sub> (1366  $\text{cm}^{-1}$ ) groups as the most reactive groups in the polymer versus the storage time. Figure 5 shows that no substantial decrease in the intensities of these bands was observed. This indicates that the oxidation of a double bond and C—CH<sub>3</sub> group does not occur.



**Figure 4** Carbonyl band (at 1730  $\text{cm}^{-1}$ ) intensity ( $D$ ) in the IR spectra of PTMSP films versus the storage time at room temperature. The film thicknesses were (1) 10 and (2) 30  $\mu\text{m}$ .



**Figure 5** Intensity of the bands ( $D$ ) at (1,3) 1365 and (2,4) 1548  $\text{cm}^{-1}$  in the IR spectra of PTMSP films versus the storage time at room temperature. The film thicknesses were (1,2) 10 and (3,4) 30  $\mu\text{m}$ .

The content of dialkyl phthalates in the stored PTMSP samples was calculated with the carbonyl band intensity in the spectrum of the PTMSP films exposed to DBP vapors. The phthalate concentration in the PTMSP films (30  $\mu\text{m}$  thick) stored for 2 years in air was about 13 wt %. The same content was reached in a PTMSP film of similar thickness exposed to DBP vapor for 4 days at a room temperature. DBP was completely extracted from the PTMSP films (even those that absorbed 20% DBP) by ethanol for 2–3 h. The chemical stability of a PTMSP sample that had been stored as a block for 6.5 years in air at room temperature in dark was examined. The IR spectrum of the film revealed alkyl phthalate bands, which disappeared after the soaking of the film in

ethanol. No bands of oxidation products were found in this spectrum. The ethanol extraction of PTMSP films stored for 2–8 years<sup>8</sup> indicated that the new band in the IR spectra of these samples, previously assigned to oxidation products of the polymer, actually was due to dialkyl phthalates that obviously were sorbed from the environment.

Characteristic bands in the IR spectrum of PTMSP containing absorbed DBP and their assignment are listed in Table I. Table I and Figures 1 and 2 show that the most intense bands typical for DBP are due to vibrations of C=O and C–O groups. The same groups are inherent to the oxidation products of polymers, and this circumstance led to the inadequate interpretation of changes in the IR spectra of PTMSP samples during their storage.

All the presented data contradict the suggestions that oxidation is one of the main factors of PTMSP aging; the main factor of PTMSP aging is contamination, particularly with phthalates, whose vapors are easily absorbed by the polymer from air.

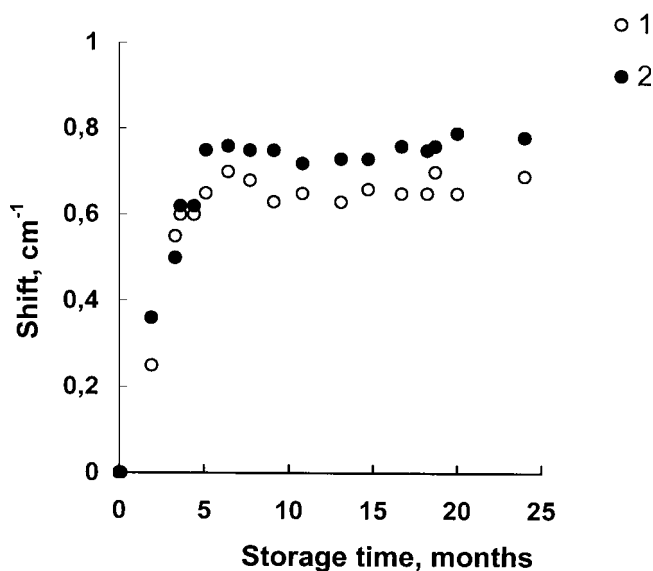
A high sorption activity of PTMSP with respect to the vapors of phthalates led us to investigate the sorption of phthalates from air and water by this polymer in more detail. This work, recently published in part,<sup>14</sup> indicated a number of useful properties of PTMSP as a possible solid-phase polymeric sorbent for the detection of dialkyl phthalates in the environment.

There are some additional IR spectral features, namely the shift of the double-bond band (1548  $\text{cm}^{-1}$ ) in PTMSP spectra during the long-term storage of polymer samples. This band is sensitive to changes in the polymer density. Thus, a reversible low-frequency shift (by 9  $\text{cm}^{-1}$ ) of this band when the temperature rose from 20 to 180°C was observed.<sup>15</sup> From a pure

**TABLE I**  
Characteristic Bands in the IR Spectrum of a PTMSP Film Containing Absorbed DBP

Frequency ( $\text{cm}^{-1}$ )	Assignment	Frequency ( $\text{cm}^{-1}$ )	Assignment
2984	$\text{CH}_3$ –(C), PTMSP	1366	$\text{CH}_3$ –(C), PTMSP
2961	$\text{CH}_3$ , DBP	1287	C–O, DBP
2956	$\text{CH}_3$ –(Si), PTMSP	1245	$\text{CH}_3$ –(Si), PTMSP
2934	$\text{CH}_2$ , DBP	1179	$\text{CH}_3$ –(C), PTMSP
2906	$\text{CH}_3$ –(Si)	1136	C–O, DBP
2874	$\text{CH}_3$ , DBP	1122	C–O, DBP
2852	$\text{CH}_3$ –(C), PTMSP	1075	C–O, DBP
1740–1730	C=O, DBP <sup>a</sup>	1025	C–C, PTMSP
1600	Aromatic, DBP	1010	C–C, PTMSP
1580	Aromatic, DBP	913	$\text{CH}_3$ –Si, PTMSP
1548	C=C, PTMSP	837	$\text{CH}_3$ –Si, PTMSP
1466	$\text{CH}_2$ , DBP	758	$\text{CH}_3$ –Si, PTMSP
1450	$\text{CH}_3$ , DBP	744	Aromatic, DBP
1431	$\text{CH}_3$ , PTMSP	705	Aromatic, DBP
1380	$\text{CH}_3$ , DBP	680	Si–C, PTMSP
		636	Si–C, PTMSP

<sup>a</sup> The frequency depends on the DBP content.



**Figure 6** Shift of the double-bond band (at  $1548\text{ cm}^{-1}$ ) in the IR spectra of PTMSP films during their storage in air at room temperature. The film thicknesses were (1) 25 and (2)  $10\text{ }\mu\text{m}$ .

PTMSP sample to a PTMSP/polyvinyltrimethylsilane (1 : 1) blend, the  $\nu(\text{C}=\text{C})$  band shifted by  $2\text{ cm}^{-1}$  to a high-frequency range at room temperature. A significantly lower shift of the  $\nu(\text{C}=\text{C})$  band from  $1548.0$  to  $1548.8\text{ cm}^{-1}$  occurred in IR spectra of PTMSP films during their storage for 2 years at room temperature. Most likely, this fact reflects the physical aging of the polymer.

Figure 6 shows the shift of the double-bond band during PTMSP film storage in air. The displacement of the  $\nu(\text{C}=\text{C})$  band takes place for the first 5 months of aging. The observed shift is likely due to an increase in the polymer density due to the relaxation and/or incorporation of plasticizer molecules.

We also observed the same results for the PTMSP samples having cis and trans units in a ratio of 40 : 60 and prepared with a  $\text{TaCl}_5$ -triisobutylaluminumoxane catalytic system.

## CONCLUSIONS

The influence of various factors (oxidation, relaxation, and sorption of low-molecular-weight compounds from the environment) on the aging of PTMSP dur-

ing long-term storage in air was investigated with FTIR spectroscopy. It was concluded that the polymer did not undergo oxidation in air at room temperature for at least 6.5 years. The absorption of plasticizer vapors (and possibly other compounds) from the environment and the reduction of the free volume due to relaxation and/or incorporation of plasticizer molecules were the main reasons found for PTMSP aging. The stability of PTMSP to oxidation in air is most likely due to the helical structure of the polymer macromolecule,<sup>16</sup> which has bulky side substitutes. Such a structure prevents the attack of oxygen against double bonds and carbon methyl groups.

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