Transport Characteristics and Other Physicochemical Properties of Aged Poly(1-(trimethylsilyl)-1-propyne)

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SYNOPSIS

Samples of poly[1-(trimethylsilyl)-1-propyne] were kept for about 4 years in ambient conditions. The permeability and diffusion coefficients were examined and found to be decreased by 1–2 orders of magnitude. To ascertain the nature of the changes underwent during long-term storage of this polymer, several physicochemical methods were applied: positron annihilation, wide-angle X-ray diffraction, spin probe, and density evaluation. These studies indicated that a decrease of free volume and more close chain packing took place during the aging process. IR spectroscopy and ^{13}C-NMR showed that oxygen-containing products appeared in the polymer after long-term storage. This should result in a certain decrease in the rigidity of the backbone chains and more intensive interchain interactions, and, hence, in a decrease in the free volume of the aged polymer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) was described in pioneer work by Masuda et al.[1] and, subsequently, drew great research interest because of its unusually high transport parameters.[2–5] This glassy polymer (its glass transition temperature is higher than 200°C[3]) is characterized by gas diffusion coefficients and permeability coefficients greater than for any known high molecular mass compound, rubbery or glassy. In particular, the permeability coefficients of this polymer for light gases (O_2, N_2, H_2, and so on) are by an order of magnitude greater than those of polydimethylsiloxane (PDMS), which has heretofore been considered the most permeable polymer. A number of other peculiarities of PTMSP—comparatively low density,[3,4] low activation energies of diffusion,[6] enhanced sorption ability, and great Langmuir capacity parameters C'_H,[3–5] great exotermicity of sorption,[4] and, last but not the least, high free-volume parameters as esti-

mated by positron annihilation and electrochromism methods[7]—can be interpreted as an indication of unusually loose packing of the chains in this polymer as a factor responsible for its specific transport properties.

Another exceptional feature of this polymer, and, besides, the one that significantly limits its practical application as a membrane material, is a rapid decrease of transport parameters in time, what has been noted by several researchers. These effects can be observed both in vacuum or inert atmosphere[8] and in the atmosphere containing oxygen or air, although the results obtained in the latter case are somewhat contradictory.[9–11]

One could relate a slow decrease in permeability with the proceeding of relaxation processes, resulting in densification of the polymer. Although the existence of relaxation processes in glassy polymers with the intrinsic times of the order of several weeks seems to be rather unusual, perhaps it cannot be excluded, taking into account the very low packing density of PTMSP as well as the existence of a domain structure in it that has been reported using the SEM technique.[12]

On the other hand, the changes in transport properties observed in the atmosphere of air or ox-

ygen can be explained by oxidizing degradation of unsaturated PTMSP. According to Odani et al.[9] and Masuda et al.,[10] heating above 120°C results in a rapid decrease of the molecular mass of the polymer. A study of PTMSP using TGA[11] showed that the rate of weight loss by the polymer is substantially higher in the atmosphere of air or oxygen than in nitrogen. Interestingly, the process is slowed down by adding of the inhibitors of radical-chain reactions. Oxidative degradation could be accompanied by depolymerization and the formation of volatile oxygen-containing products, as well as by cross-linking, that could, at least partly, explain the changes in diffusion and permeability coefficients.

At last, there have been attempts to explain the decrease in transport parameters during prolonged pumping by an artifact, namely, by sorption of vacuum oil vapors on the polymer.[5]

Thus, further work seems to be necessary to shed more light on the unusual properties and behavior of this polymer. This paper reports transport and other relevant characteristics of PTMSP after prolonged storage in the ambient atmosphere at room temperature. The properties of aged and of initial samples of PTMSP were compared and conclusions were made on structural changes of the polymer during storage.

EXPERIMENTAL

PTMSP has been prepared according to Masuda et al.[1] 1-Trimethylsilylpropyne was polymerized in toluene solution over $TaCl_5$ as a catalyst. The monomer concentration was $1 M$, and the monomer/catalyst ratio was equal to 50. Molecular masses of the polymer, determined by gel permeation chromatography (Waters, toluene, 50°C) were found to be $M_w = 590,000$, $M_n = 125,000$, and $M_w/M_n = 4.72$. The intrinsic viscosity of the polymer was equal to 4.2 dL/g. Transport and thermodynamic properties of this polymer were described in detail by Platé et al.[13]

Films of PTMSP, free of any special stabilizer, were obtained by pouring a 1–2% toluene solution onto a horizontal cellophane surface with subsequent slow evaporation of the solvent at ambient conditions. The films were dried in air at 25°C for 200–500 h and then in vacuum until constant weight was achieved.

The permeability (P) and diffusion (D) coefficients were measured using a mass-spectrometric method that has been described elsewhere.[14] In this method, the permeability coefficient is determined by the slope of the increase of a certain ion current in the mass spectrum of the diffusing gas molecule after attaining a steady-state condition, whereas the diffusion coefficient was measured by the time-lag procedure. The measurements were carried out at 22°C and at pressures of 10–100 mmHg over the membrane and about 10^{-4} mmHg below the membrane. In no case was a significant pressure dependence observed for the permeability and diffusion coefficients; therefore, the values reported can be considered as averaged over this pressure range. The accuracy of determination of P values was about 10–15%; D values were measured with somewhat lower accuracy (20–25%).

The positron lifetimes were measured on a standard instrument Ortec (U.S.A.), which had a resolution function with the full width at half-maximum (fwhm) equal to 300 ps. The radioactive isotope ^{22}Na was used as a source of positrons; it had an activity of about 10 μCi. The spectra were treated on a computer using a program with an automatic selection of the parameters of the resolution function and account for the contribution into the lifetime spectrum from the annihilation in the material of the source. All the data reported here were obtained at 22 $\pm$ 2°C. The positron source was sandwiched by two stacks of the sample polymer films having 10 mm in diameter and a thickness of about 40 μm, the overall thickness of the stack being equal to 2 mm.

The wide-angle X-ray study was performed with filtered CuKα radiation using an IRIS-O device and a DRON-3M X-ray diffractometer (CuKα) with an asymmetric focusing monochromator (a bent quartz crystal), equipped with a heating camera wherein the temperature was automatically regulated ($\pm$1°C). A statistical treatment of the results[15] showed that the error in determining the angular position of the amorphous halo maximum did not exceed 0.05°.

The stable free-radical 2,2,6,6-tetramethyl piperidine-1-oxide (TEMPO) was used as a spin probe by ESR investigation of initial and aged PTMSP. TEMPO was introduced into polymer films from a vapor phase. The samples with the spin probe sorbed were sealed in glass ampules, where they were stored until the signal characteristic for a surface adsorption state of the probe had not vanished and the spin probe was uniformly distributed within the sample, a standard procedure for the spin probe method.[16] ESR spectra were recorded on a Bruker instrument in the 3 cm range in conditions far from saturation, i.e., when correlation times τ_c of the probe are limited in the range $5 \times 10^{-11} - 10^{-7}$ s. Correlation times were calculated using the equation

$$\tau_c = 6.65 \Delta H [(I_{+1}/I_{-1})^{1/2} - 1] 10^{-10}$$

where ΔH is the line width (in Gauss) of the high-field component, and I_{+1} and I_{-1}, the intensities of the low- and high-field components, respectively. For the range $\tau_c = 10^{-9} - 7 \times 10^{-9}$, correlation times were corrected using the nomogram from Ref. 17.

DSC measurements were carried out in a Mettler instrument in the range 20–250°C at a scan rate 10 K/min. IR spectra were recorded using a Perkin-Elmer spectrophotometer, Model 577. The samples were prepared in a form of the films with a thickness of about 20 μm cast from toluene solutions.

An NMR spectrometer Bruker MSL-300 having a working frequency 300 MHz CH was used to characterize the structure of the initial and aged PTMSP. The spectra were recorded for the polymers dissolved in $CDCl_3$ with 98% content of deuterium. Recording was carried out in the pulse mode regime with Fourier transform. A method of full broad band decoupling of the signals of carbon atoms and protons was employed by recording ^{13}C NMR spectra. The measurements were performed at 25 ± 3°C with stabilization by the deuterium signal of the solvent.

RESULTS AND DISCUSSION

The samples of PTMSP that had been investigated earlier[4,13] were stored for 4 years in ambient atmosphere (temperature 22 ± 3°C). During this period, initially, colorless samples acquired a tint of yellow.

Solubility

After storage, the samples of PTMSP kept the solubility in hydrocarbon solvents typical for this polymer in its initial form. Thus, it can be assumed that during the storage no substantial cross-linking of the polymer took place. The samples of PTMSP were dissolved in toluene and new films having the thickness about 100 μm were cast from the solution.

Density

Several types of density ρ were measured and reported for initial PTMSP.[4,13] A so-called geometric density can be estimated by weighing the samples of a regular form (e.g., discs with known diameter and thickness). By such an estimation of the density, the greatest error is introduced by the measuring of the thickness. Accordingly, the error in the determination of geometric density can be as great as 10% for the samples with a thickness of about 30

μm. For different samples, the geometric density was in the range 0.61–0.77 g/cc (the average value, 0.71 ± 0.07 g/cc). The measurement of the density by gradient columns (the mixture diethylene glycol-ethanol) gave a significantly higher value: 0.964 g/cc. It is known that this method can give a series of systematically higher values of the density in comparison with geometric density due to sorption of the solution during the slow process of the measurement of the density. Rather close values of the density have been reported in the literature: 0.75 (Refs. 2 and 3) and 0.78 g/cc (Ref. 5), although it is not always clear on what type of the measurement these values are based.

For the sample of aged PTMSP free of solvent, the geometric density was found to be equal to 0.910 ± 0.09 g/cc. Testing this sample by hydrostatic weighing (liquid phase of a known density: propanol-1) gave the value of 1.05 g/cc. Since the procedure of weighing using this method is very quick in comparison with weighing in the gradient column (less than 1 min), one can anticipate rather a low degree of bulk sorption; therefore, the close coincidence of two values seems to be reasonable.

Thus, long-term storage of PTMSP in ambient atmosphere results in a substantial, by 20–30%, increase in the density of the polymer. This conclusion is in qualitative agreement with the estimation of a rather high free-volume fraction for fresh PTMSP reported earlier.[6,7] A similar evaluation can be made if one estimates the van der Waals volume of the repeat unit of PTMSP using the method of group contributions and postulates according to Bondi[18]: that the occupied volume of a polymer $v_{oc} = 1.3 \, v_w$. Then, the free volume (v_f) or free-volume fraction (v_f/v_{sp}) can be estimated, where $v_{sp} = 1/\rho$ and $v_f = v_{sp} - v_{oc}$. Such an estimation gives for initial PTMSP an exceptionally high value of free-volume fraction equal to 36%; whereas for aged PTMSP, it is much lower: 19%.

Gas Permeability and Diffusion

Figure 1 shows the permeability coefficients for initial and aged samples of PTMSP. It is seen that P values decreased for all the gases approximately by one order (by 6–27 times). A somewhat more drastic decrease can be observed for so-called slow gases like N_2 or CH_4; therefore, a certain increase in separation factors $\alpha(H_2/N_2)$, $\alpha(H_2/CH_4)$, and $\alpha(CO_2/CH_4)$ can be noted (Table I). The values presented in Figure 1 show that in spite of the decrease in permeability for aged PTMSP this polymer is still in the group of the most permeable polymers. Thus,

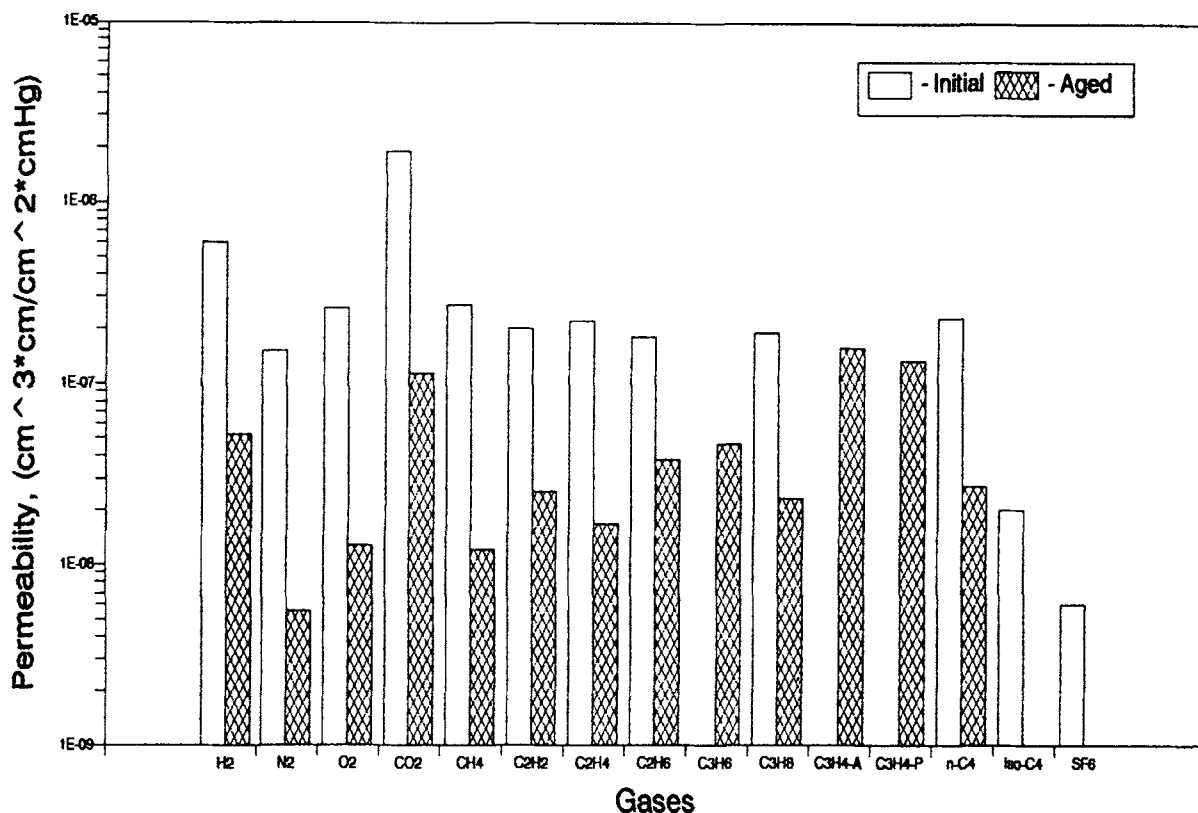## Permeability of Gases in PTMSP

Figure 1 Permeability of initial and aged PTMSP (C_3H_4-A, allene; C_3H_4-P, propyne).

the observed permeability coefficient for H_2 in this polymer is close to the one reported for PDMS[19] and by a factor 2.5 higher than the P value for highly permeable glassy polymer: polyvinyltrimethylsilane (PVTMS).[20]

A specific feature of PTMSP is a high rate of gas diffusion and, hence, very short time lags. Thus, for the films having thickness of 200 μm investigated

Table I Separation Factors α_{ij} in the Initial and Aged PTMSP

M_i/M_j	Initial	Aged
O_2/N_2	1.7	2.3
H_2/N_2	4.0	9.6
H_2/CH_4	2.2	4.4
CO_2/CH_4	7.0	9.3
C_2H_2/C_2H_4	1.0	1.5
C_2H_2/C_2H_6	1.1	0.7
C_2H_4/C_2H_6	1.2	0.4
Allene/C_3H_8	—	6.7
Methylacetylene/C_3H_8	—	5.7

by Stern et al.,[3] the time lags corresponding to the reported D values should be equal to 2–3 s, which is not so easy to measure. It was found for aged PTMSP that time lags have an order of several hundred seconds, so they can be measured with confidence for a number of gases. Figure 2 shows D values for gases as a function of the molecular size, the optimized scale for which has been given by Teplyakov.[21] The diffusion coefficients are compared for aged and initial samples of PTMSP. It is seen that for all the gases the values of diffusion coefficients are as much as about two orders lower than the corresponding D values for initial PTMSP. Meanwhile, the slow dependence of D on the molecular sizes of diffusants that has been observed earlier for initial samples of PTMSP[3,5,22] holds for the aged state of this polymer as well. One can speculate that the steepness of a size-dependence of diffusion coefficients in polymers can be related to the intrinsic size of the free-volume elements. Since the diffusion in rubbers is controlled by segmental mobility, the small slopes of the penetrant-size dependence or low size selectivity of diffusion in rubbers can be ex-
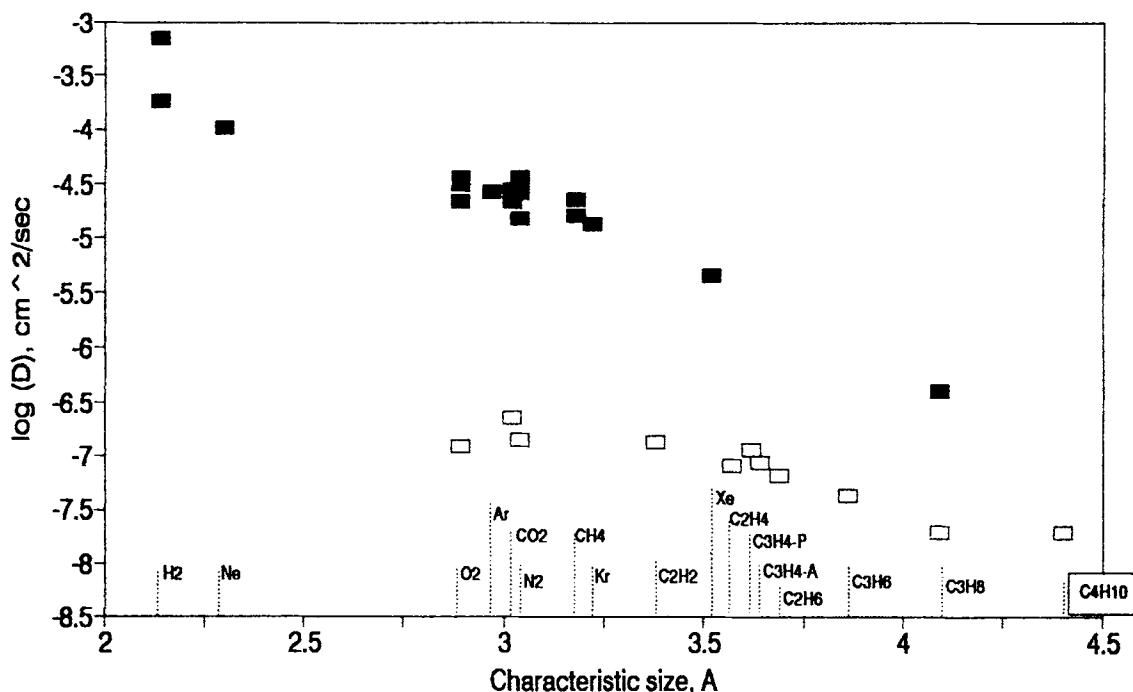
Figure 2 Diffusivity of initial (■) and aged (□) PTMSP (C_3H_4-A, allene; C_3H_4-P, propyne).

plained by the great dimension of the free-volume element in rubbers comparable to the kinetic segment. Accordingly, the weak penetrant-size dependence of the diffusivity in PTMSP could be considered a manifestation of very large free-volume sizes in this glassy polymer. Although a substantial decrease in diffusivity is observed in aged PTMSP, the penetrant-size dependence for this polymer lets one assume that the dimensions of free-volume elements in this polymer are still much greater in comparison with the sizes of diffusing gas molecules.

Positron Annihilation Measurements

This method has been used successfully for the characterization of free volume in polymers.[23] Therefore, it was interesting to apply it to such an object as PTMSP and to compare lifetimes in initial and aged samples of PTMSP. Table II shows lifetime spectra for these two polymers and, for comparison, the lifetime spectrum for PVTMS, since it has a similar chemical structure and transport characteristics close to those found for aged PTMSP. It is well known that positron annihilation lifetime

spectra for different polymers, both glassy and rubbery, consist usually of three components: τ_i, I_i, where τ_i is the lifetime of the component "i" and I_i is the corresponding statistical weight. It has been shown[23] that the long-living component τ_3, I_3 can be ascribed to free-volume elements through which gas diffusion proceeds. The comparison of PTMSP with PVTMS (and other polymers as well) indicates that the "super long-living" component appears in the spectrum having $\tau_4 = 6668$ ps. At the same time, the component τ_3 is shifted to the shorter lifetimes or smaller sizes of free-volume elements. Meanwhile, the sum of the statistical weights $I_3 + I_4$ does not differ significantly from the I_3 value in PVTMS.

Such long lifetimes of positrons as τ_4 registered for PTMSP are not quite typical for polymers but have been observed in porous solids like sorbents or catalysts, e.g., for zeolites and silicagels.[24,25] Thus, the comparison of positron annihilation spectra in PVTMS and other polymers, on the one hand, and that in PTMSP, on the other hand, suggests that there are the elements of free volume in the latter with the sizes somewhat greater than those in other polymers and similar to the "holes" or "windows" in silicagels and zeolites.

Table II   Lifetime Spectra Parameters of Positron Annihilation[a]

Polymer	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	τ_4 (ps)	I_4 (%)
PTMSP (initial)	210	41	580	25	2468	5	6668	30
PTMSP[b]	234	33	434	44	1655	7.8	3795	15
(aged)[c]	294	62	727	19	3506	18	—	—
PVTMS	205	36	698	22	3512	42	—	—

[a] τ_i, lifetime; I_i, statistical weight.
[b] Treatment of the spectrum in four components ($x^2/\nu = 1.06$).
[c] Treatment of the spectrum in three components ($x^2/\nu = 1.14$).

The aging of PTMSP results in a significant decrease in lifetimes τ_3 and τ_4, as well as in the corresponding statistical weight I_4. Aged PTMSP does not differ noticeably from other polymers if one considers τ_3 and τ_4 values: Although the treatment of the lifetime spectrum for three components leads to the statistical criterion x^2/ν somewhat worse than by the treatment for four component spectrum, it results in τ_3 values close to ones found for polymers having the highest diffusion and permeability coefficients: PDMS, poly(phenylene oxide), and PVTMS.[23]

Thus, the investigation of the aging of PTMSP by the positron annihilation method revealed a decrease of the free volume, presumably, due to denser chain packing and/or more intensive interchain interactions, which is reflected not only in the changes of the density, gas diffusion, and permeability coefficients, but also in the lifetimes of positrons in this polymer.

X-ray Scattering

Wide-angle X-ray patterns are shown in Figure 3. In both cases, X-ray diffractograms consist of three diffusive maxima. Two amorphous halos are observed for the initial PTMSP with the maximum positioned at the scattering angles $2\theta = 10.0$ and $28°$, which correspond to the periodicity of about 10 and 4 Å. The width of the first peak is equal to $3.5°$. A close value of the position and the width of the first peak ($9.5°$, $3.7°$) has been reported by Masuda et al.[26] The first of the values found here characterizes the interchain periodicity. For the aged PTMSP, the pattern does not change qualitatively, although a shift in scattering angles can be observed to higher values: For the first maximum, $2\theta = 10.4$, which corresponds to the decrease of interchain distance by 1 Å or from 10.0 to 8.9 Å. It should be noted that it

is a significant drop in the angle of scattering, comparable, for instance, with the change of interchain distance by crystallization of amorphous part of polyethylene. The changes of the interchain spacing found agree with the increase in the density of PTMSP. No changes were observed in the half-width of the peaks that could indicate the differences in ordering in initial and aged samples of the polymer. The diffusive character of the reflections (relatively large half-width and low intensity) is indicative only of the existence of the local order in both polymers, i.e., the initial and aged forms of PTMSP alike are amorphous polymers. Hence the observed changes in transport parameters cannot be explained by crystallization during long-term storage of this polymer. The weakest maximum at $2\theta = 20°$ presumably is related to the second order of reflection.

Differential Scanning Calorimetry

A peculiarity of PTMSP is a very rigid main chain and this is displayed in the high glass transition temperature of this polymer, at least higher than $200°C$.[3] Nakagawa et al.[27] reported the changes in physical properties induced by the bromination of PTMSP when the double-bond concentration decreased due to the addition of bromine atoms. Accordingly, the stiffness of the main chain of the polymer decreases and this is manifested in a substantial decrease in T_g values that are as low as $50°C$ for the polymers containing 3–13% of bromine. Since partial saturation of the double bonds can also be expected during long-term storage of PTMSP, it was interesting to test whether any transitions appear in DSC thermograms of aged samples. However, they revealed phase transitions neither of the first nor of the second order in the range 20–250°C. The same conclusion can be drawn after repeating runs in the heating or cooling regimes.
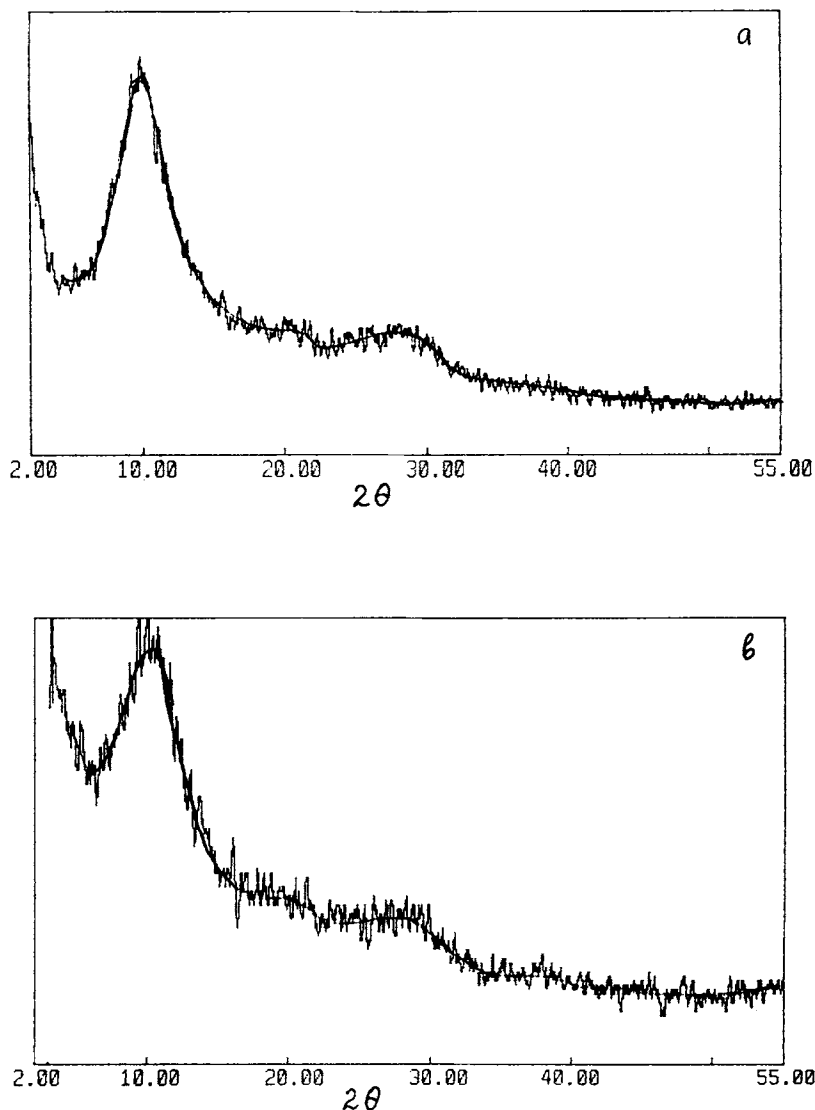
Figure 3 X-ray diffractograms for (a) initial and (b) aged PTMSP.

Spin Probe Method

Earlier it was shown[28] that the mobilities of spin probes correlate with gas diffusion coefficients in polymers. In some cases, the mobility or rotation frequency, ν_c, of the spin probe can be used for an approximate estimation of free-volume size.[29] Consequently, the changes in properties of PTMSP induced during the aging process were studied using the spin probe method. ESR spectra of the nitroxide radical TEMPO were measured in aged PTMSP and, for comparison, in PVTMS and PDMS as well. The frequencies of the rotation ν_c, defined as $\nu_c = 1/\tau_c$, are summarized in Table III. For initial samples of PTMSP, it was estimated using the

correlation[28] with gas diffusion coefficients mentioned above. The table contains also the diffusion coefficients for the polymers considered. It is evident that the mobility of TEMPO is noticeably depressed in aged PTMSP if one compares it with the initial specimen of PTMSP. The values of τ_c in PVTMS and aged PTMSP are very close, which is in agreement with other findings of the present paper.

Thus, we may establish that the samples of non-stabilized PTMSP subjected to long-term storage in room conditions revealed a decrease in gas transport parameters as well as certain changes in other physical properties. Table IV summarizes the character of changes of different properties induced by aging. It is noteworthy that all the methods of testing gave

Table III   The Frequencies of Spin Probe Rotation ν_c and Diffusion Coefficients

Polymer	$10 \, g \, \nu_c$ (s^{-1})		$D_i \cdot 10^7$ (cm^2 s^{-1})[b]			
	Exp	Calcd[a]	N$_2$	CO$_2$	CH$_4$	C$_2$H$_6$
PTMSP (initial)	—	10.3	150	250	160	—
PTMSP (aged)	8.9	8.9	1.4[c]	2.2[c]	—	0.65[c]
PVTMS	9.0	8.9	3.6	5.2	1.0	0.13
PDMS	9.95	10.3	150	110	110	62

[a] Estimation according to Ref 28.
[b] Refs. 3, 19, 20, and 22.
[c] The results of present paper.

similar results, indicating that the main reason of the decrease in diffusion and permeability coefficients is a lowering of free volume and interchain spacing.

To ascertain what the chemical transformations are, if any, that caused so dramatic changes in numerous transport and physical properties of PTMSP IR spectroscopy and ^{13}C-NMR spectroscopy were used.

IR Spectroscopy

The spectrum obtained for the initial sample of PTMSP was similar to one described earlier.[10,30] A relevant part of the IR spectrum of aged PTMSP is presented in Figure 4. The comparison of the spectra of the initial and aged samples in the whole range of wavenumbers (200–4000 cm^{-1}) revealed their identity with but one important exception: An intensive band at 1740 cm^{-1} appeared for the aged polymer that may be ascribed to the stretching vibration of C$=$O groups. The relative intensity of this band increased at least by an order of magnitude (the band at 1370 cm^{-1} responsible for methyl groups absorption being chosen as the inner stan-

dard). We found no OH absorption bands in the vicinity of 3400 cm^{-1} for aged PTMSP. The same absorption band has been observed by the thermal degradation of monosubstituted polyacetylenes[10] as well as an OH absorption band at 3425 cm^{-1}. On the other hand, Masuda et al.[10] did not find these absorption bands in PTMSP that was kept for 3 months at room temperature.

NMR Spectroscopy

A signal corresponding to a carbon atom in carbonyl groups was found in the ^{13}C-NMR spectrum. Its intensity, in respect to carbon atoms of the main chain, indicated that the content of carbonyl groups did not exceed 5%. Much more intensive signal corresponding to 20–25% content was found in the range of 120–130 ppm, which could be ascribed to various combinations of carbon atoms single-bonded to oxygen: C — O — R, C — O — O, etc. Besides that, a group of weak and only partly resolved signals (5%) appeared in the aliphatic range, probably corresponding to low molecular mass degradation products. All these patterns were absent in the spectrum of initial PTMSP. Thus, the results of spectral studies of aged PTMSP let one to conclude that a partial saturation of the main chain of this polymer takes place during slow aging. The appearance of several oxygen-containing groups, whose structures are given below, is in accord with the spectral data:

Table IV   Summary of the Changes of PTMSP due to Aging (4 years, air, 22–23°C)

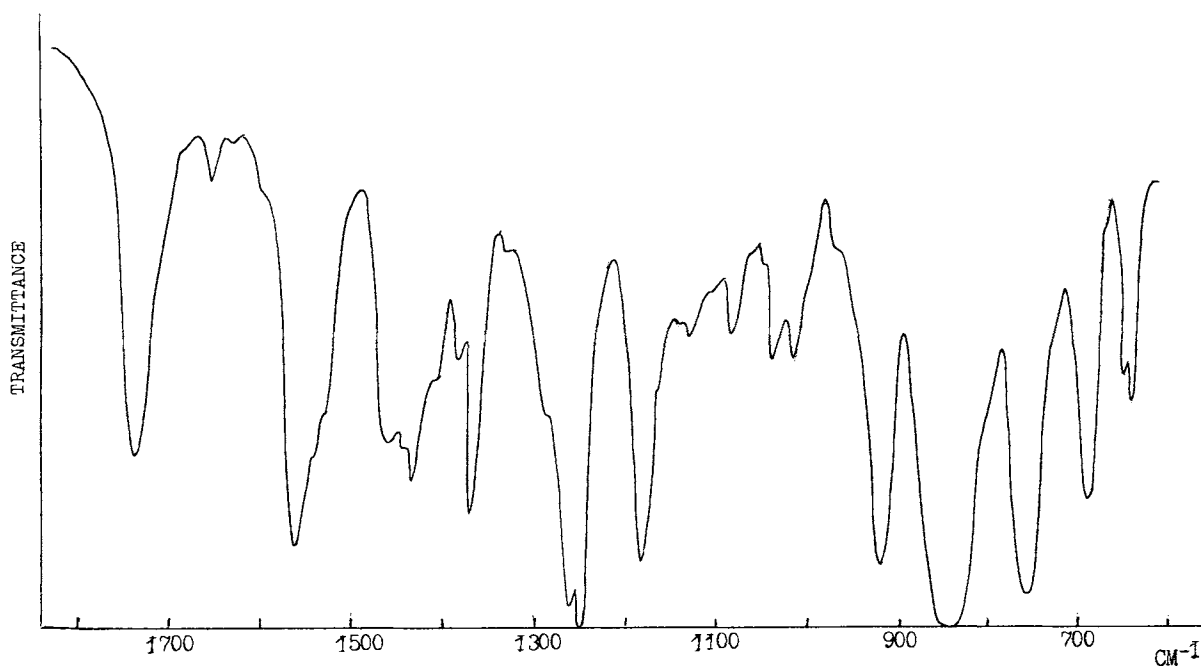| Parameter (Method)	Changes
Permeability	↘
Permselectivity	↗
Diffusivity	↘
Density	↗
Spacing (WAXD)	↘
Free volume (PA)	↘
Spin probe mobility (ESR)	↘
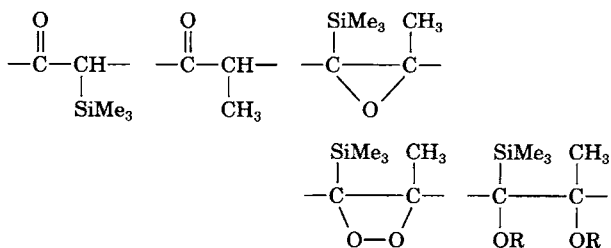
Figure 4   IR spectrum for aged PTMSP.

CONCLUSIONS

One of the important demands that can be placed upon the polymeric materials for gas-separating membranes is the stability during their storing or use in a separation process. It is well documented in the literature that changes of transport, thermodynamic, and other properties of PTMSP exposed to inert or chemically active atmosphere can be explained, in principle, by the proceeding of various physical and/or chemical transformations of this unusual polymer. The results obtained in the present paper indicate that, in spite of its rather high chemical stability in regard to oxidation processes,[10] nonstabilized PTMSP, when stored or being used for the separation of oxygen-containing gases, can undergo certain chemical transformations resulting in a decrease of free volume and in a growth of a density and interchain spacing. Interestingly, the aged polymer containing carbonyl, ether, and, perhaps, even peroxide moieties does not lose the ability to be soluble in hydrocarbon solvents. One may speculate that the absence of the cross-links, which, had they appeared, would result in an insoluble polymer, can be due to the very loose packing of the main chains of PTMSP.

The changes that the structure of PTMSP underwent during long-term storage led to the dramatic drops of permeability and diffusion coefficients.

Nevertheless, this polymer even in its aged form remains in the group of the most permeable polymeric materials known. It is quite interesting that there is a similarity of the transport properties of aged PTMSP and PVTMS. Therefore, it confirms the suggestion made earlier[4,13] that it is the higher stiffness of the polyene main-chain PTMSP that is responsible for the higher level of transport parameters in this polymer. Indeed, the main chains of PTMSP become partly saturated in the process of aging, which enables more dense chain packing. Dipole-dipole interactions between appearing side-chain oxygen-containing groups will favor the denser packing as well. On the other hand, it is difficult to explain the absence of glass transitions on DSC thermograms obtained for aged PTMSP. Let us mention once more that analogous saturation of the main chains of PTMSP by bromination have resulted in significant decrease in the stiffness and appearance of glass transition at rather low temperature.[27]

The very low permselectivities of initial PTMSP for many gas pairs make it unattractive as a membrane material for a number of gas separation problems. The growth of α_{ij} values observed for aged PTMSP while keeping a comparatively high level of permeability, good film-forming properties, and solubility makes one regard the mild chemical modification of this polymer, and not only surface mod-

ification of membranes prepared from PTMSP, as one of perspective routes to produce polymeric materials for membranes distinguished by a favorable combination of permeability and permselectivity.

REFERENCES

1. T. Masuda, E. Isobe, T. Higashimura, and K. Takada, *J. Am. Chem. Soc.*, **105**, 7473 (1983).
2. K. Takada, H. Matsuya, T. Masuda, and T. Higashimura, *J. Appl. Polym. Sci.*, **30**, 1605 (1985).
3. Y. Ichiraku, S. A. Stern, and T. Nakagawa, *J. Membr. Sci.*, **34**, 5 (1987).
4. A. K. Bokarev, V. V. Volkov, N. E. Kaliuzhnyi, E. G. Litvinova, V. S. Khotimskii, and Yu. P. Yampol'skii, *Dokl. Acad. Sci. USSR*, **305**, 117 (1989).
5. L. C. Witchey-Lakshmanan, H. B. Hopfenberg, and R. T. Chern, *J. Membr. Sci.*, **48**, 321 (1990).
6. S. R. Auvil, R. Srinivasan, and P. M. Burban, Preprints, in *International Symposium "Membranes for Gas and Vapor Separation"*, Suzdal, 1989, NPO "Polymersintez," Vladimir, p. 19.
7. Yu. P. Yampol'skii, V. P. Shantorovich, F. P. Chernyakovskii, A. I. Kornilov, and N. A. Plate, *J. Appl. Polym. Sci.*, **47**, 85 (1993).
8. H. Odani, H. Shimomura, K. Nakanishi, T. Masuda, and T. Higashimura, in *Japan–U.S. Polymer Symposium*, 1985, Abstracts, 2C19, p. 251.
9. H. Odani, H. Shimomura, K. Nakanishi, M. Kurata, T. Masuda, and T. Higashimura, *Kobunshi Ronbunshu*, **43**, 747 (1986).
10. T. Masuda, B.-Z. Tang, and T. Higashimura, *Macromolecules*, **18**, 2369 (1985).
11. M. Langsam and L. M. Robeson, *Polym. Eng. Sci.*, **29**, 44 (1989).
12. Y. Fujii, Y. Fusaoka, M. Aoyama, E. Imazu, and H. Iwatani, in *Preprints, 6th International Symposium "Synthetic Membranes in Science and Industry,"* Tuebingen, 1989, Frankfurt am Main, DECHEMA, p. 71.
13. N. A. Plate, A. K. Bokarev, N. E. Kaliuzhnyi, E. G. Litvinova, V. S. Khotimskii, V. V. Volkov, and Yu. P. Yampol'skii, *J. Membr. Sci.*, **60**, 13 (1991).
14. Yu. P. Yampol'skii, E. G. Novitskii, and S. G. Durgaryan, *Zavod. Lab.* **46**, 256 (1980).
15. Yu. K. Ovchinnikov, E. M. Antipov, G. S. Markova, and N. F. Bakeyev, *Makromol. Chem.*, **177**, 1567 (1976).
16. A. M. Vasserman and A. L. Kovarskii, *Spin Probes and Labels in Physical Chemistry of Polymers*, Moscow, Nauka, 1986.
17. L. I. Anziferova, A. M. Vasserman, A. N. Ivanova, V. A. Lifshitz, and N. S. Nazemets, *Atlas of ESR Spectra of Spin Labels and Probes*, Moscow, Nauka, 1977.
18. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
19. W. L. Robb, *Ann. N.Y. Acad. Sci.*, **146**(1), 119 (1968).
20. V. V. Teplyakov, A. L. Evseenko, E. G. Novitskii, and S. G. Durgaryan, *Plast. Massy*, **5**, 49 (1978).
21. V. V. Teplyakov, *Zh. V. Kh. O. Mendeleev*, **32**, 693 (1987).
22. T. Masuda, Y. Iguchi, B.-Z. Tang, and T. Higashimura, *Polymer*, **29**, 2041 (1988).
23. V. V. Volkov, A. V. Gol'danskii, S. G. Durgaryan, V. A. Onishchuk, V. P. Shantorovich, and Yu. P. Yampol'skii, *Polym. Sci. USSR*, **29**, 217 (1987).
24. Y. Ito, T. Takano, and M. Hasegawa, *Appl. Phys. A*, **45**, 193 (1988).
25. V. I. Gol'danskii, A. D. Mokrushin, A. O. Tatur, and V. P. Shantorovich, *Appl. Phys.*, **5**, 379 (1975).
26. T. Masuda, E. Isobe, and T. Higashimura, *Macromolecules*, **18**, 841 (1985).
27. T. Nakagawa, M. Sekiguchi, K. Nagai, and A. Higuchi, in *International Congress on Membranes (ICOM-90)*, Chicago, 1990, p. 824.
28. Yu. P. Yampol'skii, S. G. Durgaryan, and N. S. Nametkin, *Dokl. Acad. Sci. USSR*, **261**, 708 (1981).
29. Yu. P. Yampol'skii, A. M. Vasserman, A. L. Kovarskii, and S. G. Durgaryan, *Dokl. Acad. Sci. USSR*, **249**, 150 (1979).
30. M. Langsam, M. Anand, and E. J. Karwacki, *Gas Separation Purification*, **2**, 162 (1988).