

Estimation of Free Volume in Poly(trimethylsilyl propyne) by Positron Annihilation and Electrochromism Methods

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SYNOPSIS

The free volume of poly(trimethylsilyl propyne) (PTMSP), a glassy polymer distinguished by extremely high gas permeability and diffusion coefficients, was determined by means of two probe techniques—the positron annihilation method and the electrochromism method. Lifetime analysis of positron annihilation spectra revealed an additional long-lived component that is not typical for most of previously studied polymers. A model that has been developed earlier predicts that this lifetime corresponds to the larger size of free-volume elements having an intrinsic radius of about 6 Å. Therefore, PTMSP should be similar to porous inorganic sorbents. A comparison with the literary data for zeolites and silica gel confirms this. According to the electrochromism method, the temperature dependence of the size of free-volume elements for PTMSP is much weaker than that for regular glassy polymers like polystyrene. It was concluded that the great free volume in glassy PTMSP is associated with very loose packing of the chains. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(1-trimethylsilyl-1-propyne) (PTMSP) synthesis, which has been described by Masuda et al.,¹ has drawn great attention recently.²⁻⁴ The gas permeability coefficients (P) of PTMSP are at least 1–2 orders of magnitude higher than those of the most permeable synthetic polymers, rubbery or glassy. Additionally, it has been shown that this polymer is characterized by high diffusion coefficients (D), solubility coefficients (S), and great Langmuir hole saturation constant C'_H . This parameter of sorption isotherms is usually considered as a rough measure of the excess free volume in glassy polymers. Interestingly, for this polymer, anomalously low densities have been reported,³ which for some samples are as low as 0.7 g/cc.

It was only natural to explain all these peculiarities as the manifestation of the greater free volume

of PTMSP. Indeed, it has been assumed that the larger free volume associated with such structural features of glassy PTMSP as the rigid main chain and the bulky $\text{Si}(\text{CH}_3)_3$ side-chain group is responsible for the observed unusual properties of this polymer.²⁻⁵

Recently, so-called probe methods have been extensively used to estimate the free volume or characteristic size of its elements in glassy polymers.⁶⁻⁹ This work presents the results of the study of PTMSP by means of the positron annihilation method and the electrochromism method. For comparison, two other polymers were studied. The first, poly(vinyl trimethylsilane) (PVTMS) is a vinylic-type polymer having the same side-chain group as has PTMSP attached directly to main chain. Transport and thermodynamic properties of PTMSP and PVTMS have been compared earlier.^{3,10} The other polymer, polystyrene, was considered as a “typical” glassy polymer whose transport and other physicochemical properties have been extensively studied, including the investigations by means of positron annihilation and electrochromism methods.

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BACKGROUND

Positron Annihilation Method

The lifetime spectrum of positrons gives information on the defectness or free volume of a medium, e.g., a polymer, where annihilation takes place. Getting into a medium, a positron e^+ can form positronium atom Ps . The process of positron annihilation in the form of e^+ or Ps is inhibited by the capture in structure "defects" and, therefore, should be sensitive to the nature and concentration of defects. In Refs. 11 and 12, it has been shown that before annihilation positrons are localized mainly in the regions having ordered structure, whereas positronium atoms are localized in disordered regions. Since one can distinguish in the lifetime spectra of positron annihilation the components having positron or positronium nature,¹³ it is possible to obtain information on the free volume and the concentration of its elements in the regions of ordered and disordered character. In other words, free-volume elements of larger and smaller sizes are ascribed to disordered and ordered regions, respectively.

Three components are resolved usually in positron annihilation spectra. They are distinguished by lifetime τ_i (ns) and intensity I_i (%). According to Ref. 14, the longest lifetime $\tau_3 = 2000\text{--}3000$ ns is related to the annihilation of Ps in the defects of disordered regions, whereas the intermediate lifetime $\tau_2 = 400\text{--}600$ ns is associated mostly with trapped positron annihilation in ordered regions. The component τ_1 , I_1 consists of the contributions from annihilation of free e^+ and singlet Ps and will not be considered here.

According to the model accepted in Refs. 7, 14, and 15, the calculation of the free volume can be done as follows: The concentrations of the defects in ordered (N_0) and disordered (N_d) regions can be found from the equations

$$N_0 = \nu_0/4\pi D_+ R_0 \quad (1)$$

$$N_d = \nu_d/4\pi D_{Ps} R_d, \quad (2)$$

where ν_0 and ν_d are the rates of capture of e^+ and Ps by defects, respectively; R_0 and R_d are the intrinsic radii of the defects; and D_+ and D_{Ps} are the diffusion coefficients of e^+ and Ps in the medium. It can be assumed that these diffusion coefficients do not differ greatly in various polymers. The following values are accepted: $D_+ = 10^{-1}$ cm²/s and $D_{Ps} = 10^{-4}$ cm²/s. The latter value is in agreement with the correlation D vs. d^2 , where d is the size of diffusing particles (mono- and diatomic gases).¹⁶

The free-volume fractions can be found as

$$(\nu_f)_0 = \nu_0 R_0^2/3D_+ \quad (3)$$

$$(\nu_f)_d = \nu_d R_d^2/3D_{Ps} \quad (4)$$

whereas the rates of capture ν_0 and ν_d are directly related to the parameters of positron annihilation spectra:

$$\nu_0 = (\lambda_f - 1/\tau_2)I_2/(1 - I_2 - 4/3I_3) \quad (5)$$

$$\nu_d = 4(\lambda_f - 1/\tau_3)I_3/3(1 - I_2 - 4/3I_3) \quad (6)$$

Here λ_f (s^{-1}) is the rate of positron annihilation and can be found from the following relations:

$$\lambda_f = (I'/\tau' + I_2/\tau_2 + I_3/\tau_3)/(1 - I_3/3) \quad (7)$$

$$I' = I_1 - I_3/3 \quad (8)$$

$$\tau' = \tau_1 + [\tau_1 - \tau_3/(\lambda_0\tau_3 + 1)]I_3/3I' \quad (9)$$

where the rate of singlet positronium decay λ_0 is equal to 8×10^9 s⁻¹.

Electrochromism Method

The phenomenon of electrochromism has been discovered as early as in 1939,¹⁷ but its theory was developed much later.¹⁸ It involves the effects of electric field on the absorption spectra of liquid and solid substances. The changes in absorption spectra are of two types: One is related to the Stark effect and should be manifested in spectral shifts. They give little information since absorption bands for complex organic molecules are too broad in comparison with small spectral shifts. The other type of the effects is associated with the orientation of the absorbing molecules in the electric field and resulting changes in extinction coefficients. This effect can be used for the investigation of molecular mobility in condensed media and, in particular, in polymers. With this purpose, light-absorbing molecules playing the role of probes are introduced into a polymer, and the changes in their absorption spectra induced by an electric field are followed. The information about a medium studied is being obtained under the assumption that the movements of a probe are determined by the structural peculiarity and dynamic behavior of the matrix. Therefore, it is supposed in the method that the probes do not perturb the local environment, which seems to be not always evident. However, the same assumption is made in all probe methods (e.g., the spin probe method¹⁹ or the photochromic probes technique²⁰) where the size of the

probe is presumably greater than the intrinsic size of the free volume.

The changes of the optical density ΔD are the main measured values in the electrochromism method. If the polar compounds (probes) having dipole moments not less than 2–3 Debye are dispersed in a polymer and brought into an alternating electrical field, the value ΔD will depend on the microviscosity of the medium and the frequency of the field. The time of thermal rotational mobility is of the order 10^{-12} s for the molecules of low molecular weight substances. Hence, for the fields having the frequency of the order 10^2 Hz, the orientational polarization of the probes will follow the changes of the field without delay. In other words, the ensemble of the probes is observed under such conditions in the state of equilibrium. One can define the dimensionless parameter σ , called the fraction of free probes: $\sigma = 0$ by the completely frozen mobility of the probes, and $\sigma = 1$ by the equilibrium. One of us proposed²¹ to express ΔD by the equation

$$\Delta D = \sigma^2 \Delta D_1 + \sigma \Delta D_2 + \Delta D_{34} \quad (10)$$

where the first two terms are connected to orientational polarization and the third term includes the spectral changes induced by the Stark effect. The value σ depends on the relaxational properties of the medium and the size of the probe. However, if the relaxation time $\tau \gg 1/\omega$, where ω is the frequency of the alternating field, σ does not depend on ω .

It is convenient to use the so-called linear electrochromism method for the study of glassy polymers and the estimation of free volume inside them. The sample of a polymer with the probe preliminary introduced in it is placed into two fields: permanent F_0 and alternating F_c having the frequency 240 Hz. Under the action of the former, the orientation of the dipoles takes place, and the electrochromism signal reaches the limiting value corresponding the equilibrium polarization (orientation). Normally, this process proceeds easier if the sample is heated to the glass transition temperature or somewhat lower. Without switching the field F_0 , the sample is cooled to the temperature of measurement. After switching F_0 off (while F_c remains to be switched on), the process of thermal disorientation of the dipoles begins, which is reflected as a decrease in time of the electrochromism signal (optical density) in the spectrum.

The analysis of the kinetic curves $\Delta D(t)$ or $\sigma(t)$ permits one to estimate the average size of the free-volume elements where the rotation of probes takes place provided that the kinetic curves are obtained

for several probes of different sizes. The method is based on the application of the Cohen–Turnbull model,²² according to which the probability of the formation of a cavity of free volume of the size $v > v^*$, where v^* is the size of the probe, is equal to

$$P(v^*) = \exp(-\gamma v^*/v_f) \quad (11)$$

where $\gamma = 0.5-1$ is the coefficient taking into account the overlapping of the cavities (below we will assume $\gamma = 1$). It is suggested that the fraction of free probes $\sigma(v^*)$ is directly proportional to the probability $P(v^*)$:

$$\sigma(v^*) = AP(v^*) \quad (12)$$

The process of the disorientation of probes can be envisaged according to the following stepwise model: The angle between the initial and current direction of the dipole is considered to increase proportionally to $Pn^{1/2}$, where n is the number of probes in a microcavity having the volume $v > v^*$. For the disorientation of the probe by the angle $\theta = 90^\circ$, a probe has to get into a microcavity many times. In this case, the process can be treated as a Bernoulli probability problem. At $n \gg 1$, the fraction of the probes keeping the initial orientation is equal to

$$\sigma = 0.5 - \Phi(x) \quad (13)$$

where $\Phi(x)$ is the Laplas probability integral, while x is defined by the following equation as the function of time t :

$$x(t) = (t/\tau\mathbf{P} - t_{0.5}/\tau\mathbf{P})/(t/\tau\mathbf{P})^{1/2} \quad (14)$$

Here, $t_{0.5}$ is the time when the electrochromism signal is twice smaller than an initial value and τ is the intrinsic time (a constant). Thus, if one knows the experimental curve $\sigma(t)$ for a probe having the volume v_1^* , it is possible to determine, for every t , the value of the probability integral $\Phi(x)$, and, hence, using the tabulated values of $\Phi(x)$, the values $x(t)$. To find the free volume, let us express the probability \mathbf{P} from eq. (13):

$$\mathbf{P}/\tau = x^2 t^{-1} (1 - t_{0.5})^{-2} \quad (15)$$

After logarithmating and taking into account eq. (11), one receives

$$\begin{aligned} & -\gamma v^*/v_f - \ln \tau \\ & = 2 \ln x - \ln t - 2 \ln(1 - t_{0.5}) \quad (16) \end{aligned}$$

If one defines the right-hand term in this equation as Z , the average free volume v_f can be found as the cotangent of the slope of Z vs. v^* for the series of the probe's volumes v_1^* , v_2^* , etc.

EXPERIMENTAL

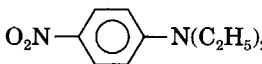
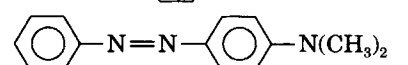
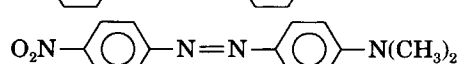
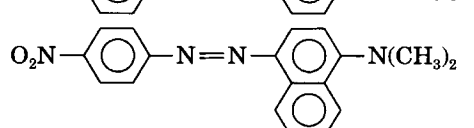
The positron lifetimes were measured on a standard instrument (Ortec, U.S.A.), which has a resolution function with the full-width at half-maximum (at fwhm) equal to 300 ps. The radioactive isotope ^{22}Na was used as a source of positrons; it had an activity of about $10\ \mu\text{Ci}$. The spectra were treated on a computer using a program with an automatic selection of the parameters of the resolution function and with account taken of the contribution into lifetime spectrum from annihilation in the material of the source. All the measurements reported in the present paper were carried out at $22 \pm 2^\circ\text{C}$. The positron source was sandwiched between two stacks of the sample polymer films of 10–15 mm in diameter and a thickness of about $100\ \mu\text{m}$. The thickness of a stack was in the range 1–2 mm. Such a procedure has an advantage in comparison with usage of monolytic discs of the same thickness since it would be very difficult to remove the traces of solvent from such massive samples. Films of PTMSP were obtained by pouring a 1–2% solution in toluene onto a horizontal cellophane surface. The films were dried in air at 25°C for 200–500 h and then in vacuum until the constant weight was achieved. The procedure of the preparation of PVTMS and polystyrene (PS) films was similar.

The technique of the investigation of polymers using the electrochromism method was as follows:

The dilute solutions of aromatic compounds, which structures are shown in Table I, and polymers (1–0.1 μmol per gram of polymer, while polymer concentration was about 1–2%) were prepared, toluene being used as the common solvent. After slow evaporation of the solvent under ambient conditions and then by drying at $50\text{--}60^\circ\text{C}$ in vacuum, the solvent can be removed completely, which was checked by spectral analysis. The film is placed between two pieces of transparent mica and two glass plates on which electroconductive and also transparent thin layers of Sn were deposited from vapor-phase decomposition of SnCl_2 at about 400°C . The sample is placed in a permanent electric field having an intensity of about $10^4\text{--}10^5\ \text{V/cm}$. At temperatures sufficiently high to provide the necessary rate of dipole orientation, one can observe an increase in optical density ΔD . The choice of the temperature at which the polarization is performed depends on the properties of a polymer, but in most cases, as has been mentioned, it is close to the glass transition temperature. On the other hand, it should not exceed 150°C because of the limited thermal stability of the azo-dyes used. In the case of PTMSP, a convenient range of temperature, interestingly, was found to be $120\text{--}130^\circ\text{C}$, i.e., much lower than the glass transition temperature for this polymer.² For the two other polymers studied, it was only somewhat lower.

The sample then is cooled to the temperature of the experiments without withdrawing the permanent field, i.e., under conditions of hindered rotation mobility of the probes. At the moment of switching the permanent field off, an anisotropism of the probes' orientation begins to decay, which is reflected by the decrease of the signal of electrochromism. According to the theory of the method,²¹ this

Table I Electrochrome Probes

<i>N</i>	Structure	$v^* \cdot 10^{22}\ \text{cm}^3$
I		7.75
II		21.8
III		27.1
IV		28.9

effect is amplified under an applied alternating electric field of low frequency (200–400 Hz). Therefore, the measurements of the molecular rotation mobility of the probes is performed under such an alternating field. More details on sample preparation and measurement have been given elsewhere.²¹

RESULTS AND DISCUSSION

Table II presents lifetime spectra obtained for PTMSP, PVTMS, and PS as well as some parameters calculated for these polymers by the same model that has been described above. Positron lifetime spectrum for PS was taken from Ref. 7, whereas that for PVTMS was measured in the present study. Since it is very close to that observed earlier,⁷ it makes the comparison of the three polymers more meaningful. As seen from Table II, the main feature of positron annihilation lifetime spectrum for PTMSP is that it consists of four components and not of three, as do all other polymers studied (see Refs. 7, 15, 23, and 24). Hence, this polymer differs from other rubbery and glassy polymers by the peculiarities of the structure determining the lifetime of positrons.

It is interesting to compare the so-called long-living component of the spectra, τ_3 , I_3 , in three polymers. The time τ_3 is significantly lower for PS

than for PVTMS. It has been shown earlier⁷ that only three polymers, PVTMS, polydimethylsiloxane (PDMS), and polyphenyleneoxide (PPO), are characterized by values $\tau_3 > 3000$ ps. All three are distinctive by large values of permeability and diffusion coefficients for gases and, presumably, by large free volume, although its nature is quite different for rubbery PDMS and glassy PPO and PVTMS. While passing from PVTMS to structurally similar PTMSP, we observe the decrease of τ_3 as well as the dramatic drop in the intensity of this component of the spectrum. Meanwhile, the fourth component, τ_4 , I_4 , of the spectrum appears with much greater time, τ_4 . It is interesting that the sum $I_3 + I_4$ for PVTMS and PTMSP are rather close. It probably means that the fourth, super-long-living component τ_4 arises at the expense of component τ_3 . So, if we assume that the existence of special structure elements in PTMSP are responsible for the appearance of the τ_4 , I_4 component of the spectrum, we are able to assume that they are formed at the expense of free-volume elements in disordered regions of the polymer^{7,14,15} while keeping the sizes and concentration of free-volume elements in so-called ordered regions nearly unchanged.

The treatment of annihilation spectra using the model described above allows us to calculate free-volume fractions corresponding to ordered and disordered regions as well as the radii of the defects or free-volume elements. The analogous calculation was performed for the fourth component of the spectrum. Some data are shown in Table II. It is seen from the table that R_3 values for PTMSP are nearly the same as for the other two polymers, while the free volume corresponding to this group of defects dramatically goes down in comparison with PVTMS. The intrinsic size R_4 of free-volume elements corresponding to the τ_4 , I_4 component is noticeably higher than those for other components of the spectra. Also, the free-volume fraction ν_{f4} is as high as it has ever been observed in positron annihilation spectra of any polymers.

Earlier it was shown⁷ that the product $\tau_3 I_3$ can be considered as a rough measure of free volume in polymer and that this value correlates with the glass transition temperatures and diffusion coefficients of gases in polymers. The advantage of this empirical approach is that it does not depend on any premises that might be included in models describing a behavior of positrons in complex media. It is seen from Table II that this approach is also applicable for the group of polymers considered in the present paper. The passage from PS to PVTMS is accompanied by

Table II Positron Annihilation Lifetime Spectra and the Parameters Calculated from Them

Parameter	Polymers		
	PTMSP	PVTMS	PS
t_1 (ps)	210	205	226
I_1 (%)	41	36	41
t_2 (ps)	580	698	543
I_2 (%)	25	22	26
t_3 (ps)	2468	3512	2130
I_3 (%)	5	42	33
t_4 (ps)	6668	—	—
I_4 (%)	30	—	—
R_3 (Å)	4.1	4.3	4.3
ν_{f3} (%)	0.6	6.2	2.5
R_4 (Å)	5.9	—	—
ν_{f4} (%)	9.1	—	—
$t_3 I_3$ (ps)	123	1475	694
$t_4 I_4$ (ps)	2000	—	—

growth of $\tau_3 I_3$ that agrees with greater gas diffusion coefficients in the latter. The fraction of free volume characterized by the value $\tau_3 I_3$ in PTMSP is minimal among all the polymers studied.⁷ Meanwhile, the fourth component of the spectrum is characterized by a high value $\tau_4 I_4$, i.e., by a great free-volume fraction.

The unusual properties of PTMSP registered by the positron annihilation method make it desirable for the search of structure analogies. Some insight into the character of this polymer can be gained by consideration of positron lifetime spectra for porous solids. The feature of positron annihilation spectra in porous media like silica gels and zeolites is the existence of their very long lifetimes (as long as 70 ns). Thus, according to Goldanskii et al.,²⁵ the lifetime of the longest component for silica gel increases with pore diameter. For the minimal pore diameter of 16 Å, the time-life reported was equal to 12,000 ps, which is only twice as great as the value τ_4 found for PTMSP. The same range of time-lives (4500–11,600 ps) has been found for different types of zeolites (Sodalite, MS-4A, Linde 13X)²⁶ having pores in the range 6.6–13 Å.

In summary, the results of this investigation of PTMSP by the positron annihilation method showed that this polymer is characterized by an unusually long lifetime of *o*-positronium and that the existence of pores having diameters of 6–12 Å can be responsible for this phenomenon.

Figures 1 and 2 show some examples of decay kinetics or normalized relaxation curves of linear

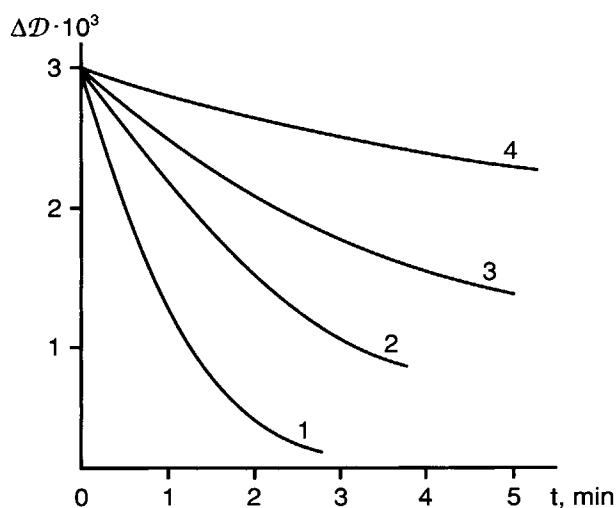


Figure 1 Decay kinetics of the signal of linear electrochromism in PS for probes 1–4 at 60°C.

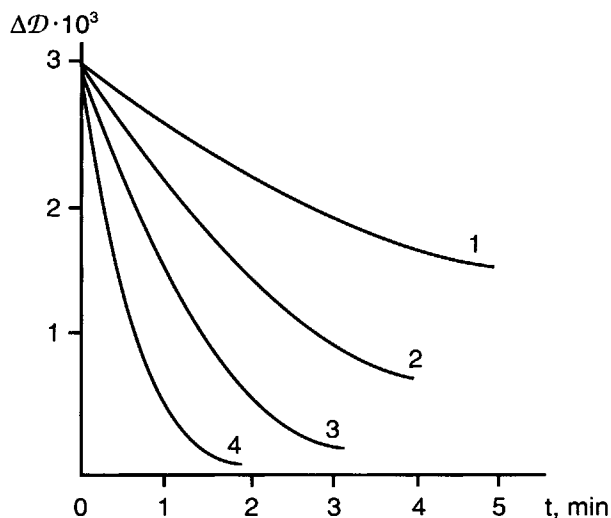


Figure 2 Decay kinetics of the signal of linear electrochromism in PS for probe 3 at the following temperatures: (1) 50°C; (2) 60°C; (3) 80°C; (4) 90°C.

electrochromism in PS. The procedure of normalization made for clarity involved recalculation of the curves to the same level ΔD at $t = 0$ (the extinction coefficients and the concentration of the probes can be somewhat different, etc.). It is seen that the rate of decline of the changes of optical density ΔD are greater the higher the temperature and the smaller the size of a probe. By using eq. (16), the sizes of the free-volume elements have been determined and are shown in Figure 3 at different temperatures for PS and PTMSP. One should keep in mind that since

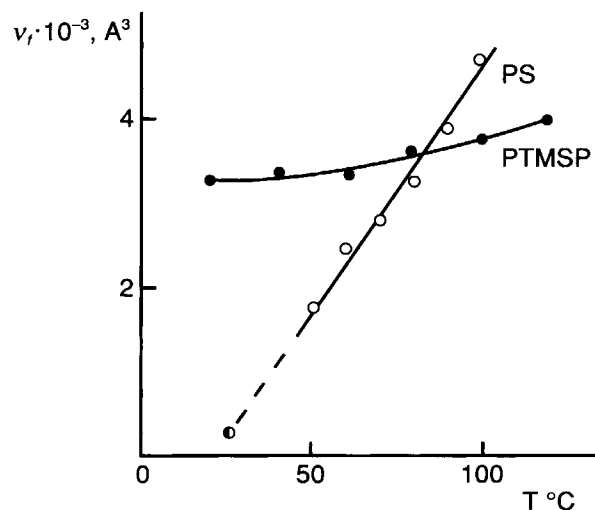


Figure 3 Temperature dependence of the size of free-volume elements in (●) PTMSP and [(○) this work; (●) Ref. 20] PS.

eq. (11) contains the intrinsic sizes of the probe used [v^* (Å^3)], therefore, v_f must be of the same dimension. It is seen from Figure 2 that at the ambient temperature the v_f value for PTMSP is much greater than that for PS. Comparison with the literature⁸ indicates that it is very much higher than the v_f observed for PVTMS or for the plastisized PS studied.

The most interesting result that is evident from Figure 3 is that entirely different temperature dependencies are characteristic for v_f in two polymers: rather steep dependence for PS and very weak changes in v_f with temperature for PTMSP. A weak temperature dependence of the free volume observed for PTMSP in contrast to the behavior of the "regular" glassy polymer—PS—can be considered as confirmation that the great free volume in this polymer is related not to the small-scale mobility of the groups but, rather, is a consequence of structure effects, i.e., loose packing of main chains. When PS approaches its glass transition temperature, v_f values become greater than those for PTMSP. In these conditions, the segmental mobility is unfreezed in PS, so the significant size of the free-volume elements seems to be reasonable.

Free volume in PS has been studied earlier by photochromic and fluorescent techniques²⁰ at ambient temperature. In this method, the amount of probe photoisomerization in a glassy polymer is measured as a function of the volume required for photoisomerization of the probe. The size of local free volume in PS found by this method is about 300 Å^3 at 25°C . It is seen from Figure 3 that this method and the method of electrochromic probes are in very good agreement.

CONCLUSIONS

Every probe method is distinguished by the dimensions of the probes employed to characterize free volume. The two methods used in the present paper are notable for use of, perhaps, the smallest possible probes (e^+ and o -Ps) in the positron annihilation method and very bulky probes in the electrochromism method. Since both methods revealed great free volume, one can assume that the size distribution of free-volume elements in PTMSP is shifted to larger sizes in both extremities in comparison with other glassy polymers. All unusual properties of this polymer (low density, small activation energy of diffusion and permeation, great exothermic effects of sorption and mixing, large Langmuir capacities parameters C'_H) are in agreement with the finding of

the present work. One can conclude that PTMSP contains in its structure pores having diameters of about 10 Å whose volume does not change significantly with temperature. It is desirable to extend this work to different polymer systems having varying structures of the main chains and side-chain groups. Temperature dependence of positron annihilation spectra for this and other structurally related polymers will be of utmost interest for understanding the mechanism of transport in highly permeable glassy polymers.

The authors are grateful to Dr. V. S. Khotimskii for supplying the samples of PTMSP.

REFERENCES

1. T. Masuda, E. Isobe, T. Higashimura, and K. Takada, *J. Am. Chem. Soc.*, **105**, 7473 (1983).
2. Y. Ichiraku, S. A. Stern, and T. Nakagawa, *J. Membr. Sci.*, **34**, 5 (1987).
3. A. K. Bokarev, V. V. Volkov, N. E. Kaliuzhnyi, E. G. Litvinova, V. S. Khotimskii, and Yu. P. Yampol'skii, *Dokl. Akad. Nauk SSSR*, **305**, 117 (1989); *Doklady, Phys. Chem.*, **305**, 189 (1989).
4. L. C. Witchey-Lacksman, H. B. Hopfenberg, and R. T. Chern, *J. Membr. Sci.*, **48**, 321 (1990).
5. S. R. Auvil, R. Srinivasan, and P. M. Burbán, in *International Symposium "Membranes for Gas and Vapor Separation,"* Suzdal, 1989, Preprints, p. 19.
6. Yu. P. Yampol'skii, in *7th European Summer School in Membrane Science*, The Netherlands, 1989.
7. V. V. Volkov, A. V. Goldanskii, S. G. Durgaryan, V. A. Onishchuk, V. P. Shantorovich, and Yu. P. Yampol'skii, *Vysokomol. Soed. A*, **29**, 192 (1987).
8. N. L. Muravieva, F. P. Chernyakovskii, Yu. P. Yampol'skii, and S. G. Durgaryan, *Zh. Fiz. Khim.*, **61**, 1894 (1987).
9. Yu. P. Yampol'skii, N. E. Kaliuzhnyi, and S. G. Durgaryan, *Macromolecules*, **19**, 846 (1986).
10. 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).
11. A. V. Goldanskii, V. A. Onishchuk, V. P. Shantorovich, and I. N. Musaelyan, *Khim. Vysokikh Energii*, **19**, 13 (1985).
12. S. J. Tao, *Appl. Phys. B*, **10**, 67 (1976).
13. J. R. Stevens, in *Polymers—Methods of Experimental Physics*, Academic Press, New York, London, 1980, Vol. 16, Part A, p. 371.
14. G. G. Aleksanyan, A. A. Berlin, A. V. Goldanskii, N. S. Grinova, V. A. Onishchuk, V. P. Shantorovich, and G. P. Safonov, *Khim. Fiz.*, **5**, 1225 (1986).
15. A. V. Goldanskii, V. A. Onishchuk, V. P. Shantorovich,

- V. V. Volkov, and Yu. P. Yampol'skii, *Khim. Fiz.*, **7**, 616 (1988).
16. V. V. Teplyakov and S. G. Durgaryan, *Vysokomol. Soed. A*, **26**, 1498 (1984).
17. W. Kuhn, H. Durkop, and H. Martin, *Z. Phys. Chem.*, **45**, 121 (1939).
18. W. Liptay and J. Czealla, *Z. Electrochem.*, **65**, 727 (1961).
19. A. M. Vasserman and A. L. Kovarskii, *Spin Probes and Labels in Physical Chemistry of Polymers*, Nauka, Moscow, 1986 (in Russian).
20. J. G. Victor and J. M. Torkelson, *Macromolecules*, **20**, 2241 (1987).
21. F. P. Chernyakovskii, *Uspekhi Khim.*, **47**, 563 (1979).
22. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1162 (1959).
23. V. I. Goldanskii, *Physical Chemistry of Positron and Positronium*, Nauka, Moscow, 1968 (in Russian).
24. A. V. Goldanskii, V. A. Onishchuk, and V. P. Shantorovich, *Phys. Stat. Sol. A*, **102**, 559 (1987).
25. V. I. Goldanskii, A. D. Mokrushin, A. O. Tatur, and V. P. Shantorovich, *Appl. Phys.*, **5**, 379 (1975).
26. Y. Ito, T. Takano, and M. Hasegawa, *Appl. Phys. A*, **45**, 193 (1988).

Received November 22, 1991

Accepted February 26, 1992