Polymer Vol. 37 No. 15, pp. 3397–3403, 1996

0032-3861/96/$15.00 + 0.00

Free volume microstructure of tetramethylpolycarbonate at low temperatures studied by positron annihilation lifetime spectroscopy: a comparison with polycarbonate

J. Bartoš*
Polymer Institute, Slovak Academy of Sciences, Dúbravská Cesta 9, 84236 Bratislava, Slovakia

and K. Krištiaková, O. Šauša and J. Krištiak
Institute of Physics, Slovak Academy of Sciences, Dúbravská Cesta 9, 84228 Bratislava, Slovakia
(Received 26 September 1994; revised 24 August 1995)

The annihilation of positrons in amorphous tetramethylpolycarbonate (TMPC) has been investigated in the temperature range from 30 to 300 K. The dependences of the mean lifetime of the *ortho*-positronium τ_3 and its relative intensity I_3 on temperature can be described by the empirical relations: $\tau_3 = 2.08(1 + 4.8 \times 10^{-4} T)$ (ns) and $I_3 = 20.2(1 + 7.9 \times 10^{-4} T)$ (%). These dependencies are interpreted within the framework of the microstructural free volume concept. The comparison with the polycarbonate (PC) reveals that both values τ_3 and I_3 are larger for TMPC, indicating larger free volume realized through higher number (concentration) of larger free volume entities. The temperature dependencies of τ_3 and I_3 for TMPC exhibit a different character and a weaker dependence on the temperature. This different behaviour of the free volume is due to a different packing efficiency of chains and a different dominant mechanism of the free volume generation, as well as a decrease in the flip dynamics of the phenyl rings. The implications of different free volume microstructures on some mechanical properties (e.g. relaxation and fracture) as well as on the transport properties of gases in TMPC and PC are discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: tetramethylpolycarbonate; positron annihilation; free volume characteristics)

INTRODUCTION

The structure of amorphous polymers is studied mainly by diffraction methods[1]. However, the basic characteristic of the disordered phase, the radial distribution function, does not provide information about the local spatial variation of the structure. Another structural quantity, the density fluctuation, reflects the inhomogeneity of the material but on a relatively large spatial scale (few tens of Å)[2–5]. Recently, the local variation of the polymer structure has become more intensely studied by means of positron annihilation methods, which enable the characterization of the so-called negative defects, such as free volume entities, on atomic level[6]. The progress in methodology and interpretation has made possible the determination of not only the average size[7] but also the free volume fraction[8] and the mean concentration of holes[9], as well as their size distributions[10]. It is evident that the complete free volume characterization is of crucial importance from the viewpoint of the generally accepted intuitive relationship between the free volume and the internal mobility of the chain segments controlling the mechanical, physical and physico-chemical properties[11–13].

The positron annihilation lifetime spectroscopy (PAL) is based on the fact that the positron lifetime is very sensitive to the existence of the structural inhomogeneities of the medium, e.g. defects and holes[14,15]. In the case of molecular substances as polymers, besides the annihilation of the positron e^+, there takes place also the formation and annihilation of the bound state of the positron with the electron, i.e. positronium Ps. The positronium Ps can exist in two states depending on the mutual spin orientation of e^+ and e^-. The singlet state of *para*-positronium (p-Ps) has a lifetime of $\tau_1 \sim 125$ ps in vacuum, the triplet *ortho*-positronium (o-Ps) annihilates in vacuum with $\tau_3 = 142$ ns. Due to the interaction of o-Ps with the electrons from the surrounding matter, in condensed media this value lowers to a few ns. It is supposed that the o-Ps is formed from the positron after its deceleration to the thermal energy and by its eventual diffusion towards the regions of lower electron density (cavity, defect or hole), where the o-Ps can then exist until the moment of its conversion into p-Ps or its annihilation. The annihilation of the o-Ps in a spherical

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* To whom correspondence should be addressed

hole can be described by a simple quantum-mechanical model of the spherical potential well with electron layer of thickness ΔR[7]. This model provides the relationship between the radius of the hole R and the o-Ps lifetime τ_3:

$$\tau_3 = \frac{1}{2}[1 - R/R_0 + (1/2\pi)\sin(2\pi R/R_0)]^{-1} \qquad (1)$$

where $R_0 = R + \Delta R$. The parameter $\Delta R = 1.656\,\text{Å}$ has been determined from fitting the experimental values of τ_3 obtained for materials with known hole size, e.g. zeolites.

Thus equation (1) allows us to determine the size of free volume entities; however, the determination of the total free volume requires the knowledge of the mean concentration of the holes $\bar{N}_h$. In our recent work[9] we have proposed a phenomenological model allowing the estimation of $\bar{N}_h$ from the combination of dilatometric data and the results from measurements of o-Ps lifetimes.

Considering the key importance of free volume characteristics, it is desirable to investigate systematically the influence of various physical and chemical factors on these characteristics. The polycarbonate of 4,4′-isopropylidenediphenol [bisphenol-A polycarbonate (PC)] belonging to the group of aromatic polymers is frequently studied due to its commercial importance[16]. Previous research on this polymer using positron annihilation which has been performed in relatively high temperature regions (above room temperature) and which has investigated the influence of thermal annealing above and below the glass transition temperature T_g (refs 17 and 18) and the linear deformation[19] have been recently completed by our study[9] in the low temperature region. However, the influence of the chemical factor, e.g. the modification of the basic chemical structure of PC on the annihilation characteristics, has been investigated in the relatively high temperature region only in ref. 20.

Tetramethylbisphenol-A polycarbonate (TMPC) is the most common modification of PC. The substitution of four hydrogen atoms by the methyl groups leads to the significant changes of physical properties such as T_g (ref. 16). Recent studies of the structure of TMPC by the small and wide angle X-ray scattering (SAXS and WAXS) methods[21] indicate that the average distance between the chains and the density fluctuations are larger than in PC, which allows one to deduce that the average free volume and the free volume fluctuations are also larger.

The aim of this work is to present the results of the influence of the chemical modification of PC on the annihilation characteristics of o-Ps in the TMPC in the low temperature region. The mean free volume quantities obtained here characterize quantitatively the different physical microstructures of PC and TMPC. The microscopic causes of these differences are discussed and the consequences of the different free volume microstructures for important mechanical and transport properties of both polymers are analysed.

EXPERIMENTAL

Sample

TMPC produced by Bayer AG, Germany, with $M_w = 4.3 \times 10^4$ and $M_n = 1.47 \times 10^4$, has been used as sample. The glass transition temperature $T_g = 203°\text{C}$ has been determined using differential scanning calorimetry (d.s.c.) with a heating rate of $20\,\text{K}\,\text{min}^{-1}$. A 3 mm thick plate has been produced from the granulate, from which disk-shaped samples with diameters of 10 mm have been prepared. Samples have been tempered at 30 K above T_g prior to measurement in order to eliminate the previous thermal history of the material.

Positron annihilation lifetime spectroscopy

The positron source ^{22}NaCl was deposited in an envelope of Kapton foils (8 μm thick). It was then sandwiched in between two identical pieces of the samples. This assembly was completely enclosed in a copper sample holder at the end of the cold finger of a closed-cycle helium gas refrigerator with automatic temperature regulation. The entire source sample assembly was kept in a vacuum. The temperature was measured at the end of the cold finger. Each selected temperature was kept constant within 1 K during the data acquisition. Several runs were performed at most of the temperature settings. Good reproducibility of the results has been obtained for each temperature. The positron annihilation lifetime spectra were obtained by the conventional fast–fast coincidence method using plastic scintillators coupled to Philips XP2020 photomultipliers. Ortec 583 constant fraction discriminators were used for selecting the energy and providing timing signals to a time-to-amplitude converter. The time resolution (FWHM) of prompt spectra was 320 ps. A model-independent instrumental resolution function was obtained from the decay curve of ^{207}Bi isotope with a single lifetime of 186 ps. The resolution function was approximated as a sum of three Gaussian distributions. In conventional analysis, the Kirkegaard *et al.* PATFIT-88 software package[22] was used to fit up to four components in the lifetime spectra. The four-component analysis gave an error in the intensity of the third component comparable to the intensity itself. All data have been corrected for the source contribution.

Next we analysed the PAL spectra taken at 293 K and 112 K as continuous lifetime distributions using the modified CONTIN program[23,24]. The constrained regularized least-squares solution of the Fredholm integral equation provided the positron annihilation rate probability density function (PDF) $\alpha(1/\tau)$. A transformation of the annihilation rate PDF, $\alpha(1/\tau)$, to the corresponding radius PDF for the free volume regions in which o-Ps annihilates is obtained from equation (1). The radius PDF is given by[23]:

$$f(R) = 3.312(\cos[2\pi R/(R + \Delta R)] - 1) \times \alpha(1/\tau)/(R + \Delta R)^2 \qquad (2)$$

This means that the fraction of positrons annihilating in cavities with radii between R and $R + \mathrm{d}R$ is $f(R)\mathrm{d}R$. The free volume PDF, assuming a spherical cavity, is given by:

$$g(V) = f(R)/4\pi R^2 \qquad (3)$$

RESULTS AND DISCUSSION

PAL results

Experimental results from finite-term lifetime analyses of amorphous tetramethylpolycarbonate in the temperature range from 30 to 300 K are presented in *Table 1* and *Figures 1* and *2*. Typical values of three-component analysis at two representative temperatures are presented in *Table 1*. The temperature dependencies of annihilation characteristics *o*-Ps are shown in *Figures 1* and *2*. The mean lifetime τ_3 and relative intensity I_3 of the *o*-Ps increase linearly with increasing temperature. Empirical relations describing these dependencies are the following:

$$\tau_3(T) = 2.08(1 + 4.8 \times 10^{-4}T) \quad \text{(ns)} \tag{4}$$

$$I_3(T) = 20.2(1 + 7.9 \times 10^{-4}T) \quad (\%) \tag{5}$$

The average hole radius R, determined by the semi-empirical model [equation (1)], is plotted on the right-hand axis of *Figure 1*. The experimental results of the continuous lifetime analysis at temperatures 112 K and 293 K are presented in *Figure 3* [the radius probability function, $f(R)$] and *Figure 4* [the volume distribution representation, $g(V)$].

Table 1 Positron and positronium lifetime results obtained by the three-component analysis in a TMPC

T (K)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	I_1 (%)	I_2 (%)	I_3 (%)
50	234 ± 9	554 ± 36	2163 ± 23	54 ± 3	26 ± 3	20 ± 4
293	214 ± 2	513 ± 5	2374 ± 3	44.7 ± 0.5	30.9 ± 0.5	24.5 ± 1

Comparison between TMPC and PC

The *o*-Ps lifetimes in TMPC are, in general, larger than those in PC in the whole temperature range investigated. This means that the mean size of the free volume entities in TMPC is larger and ranges from 110 to 135 Å^3, as compared with the values of 80–110 Å^3 observed in PC. It is noteworthy that this range of free volume magnitudes corresponds to 37–43% of the van der Waals volume of the structural unit $V_w = 299$ Å^3 in TMPC and to 33–50% of the value for $V_w = 230.5$ Å^3 in PC. This is a consequence of the chemical modification of the structural units leading to a decreased packing efficiency on a local level of certain structural units forming the specific hole. This conclusion is supported by the comparison of the functions $f(R)$ or $g(V)$ shown in *Figures 3* and *4* with the distributions obtained on PC in our recent work[25]; e.g. comparison of the room temperature distributions for TMPC with those of PC shows not only a higher maximum but also a broader distribution of volumes in TMPC, although both curves start off at practically identical values.

The qualitatively different character of distributions in TMPC compared with those of PC requires a more detailed analysis, which shall be presented elsewhere.

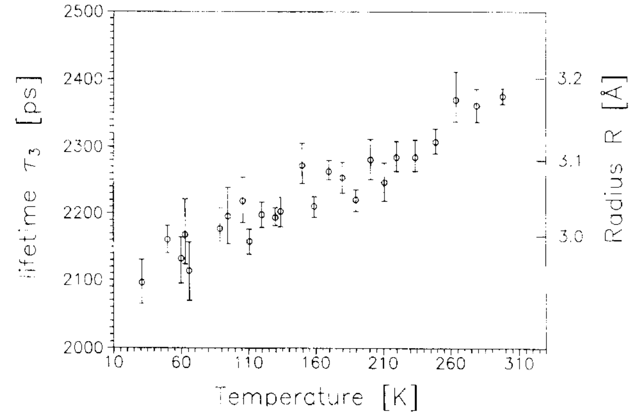

Figure 1 Mean *o*-Ps lifetime τ_3 as a function of temperature T in TMPC

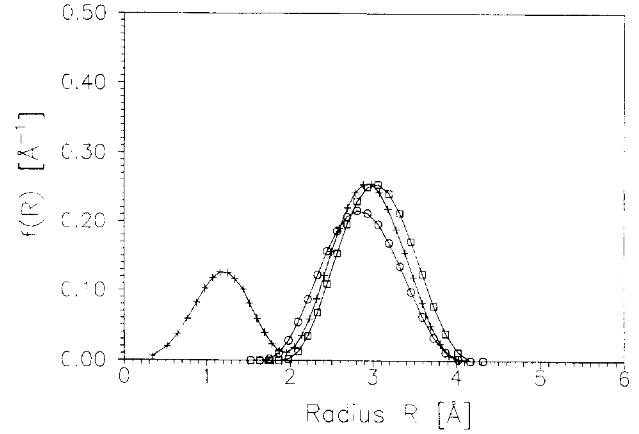

Figure 3 Free volume hole radius distributions $f(R)$ of polycarbonate (+, at 293 K) and tetramethylpolycarbonate (□, at 293 K; ○, at 112 K). Smooth curves are drawn through data points for clarity

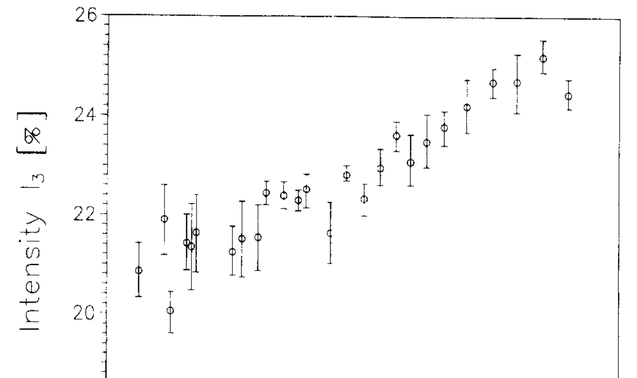

Figure 2 Intensity I_3 of *o*-Ps as a function of temperature T in TMPC

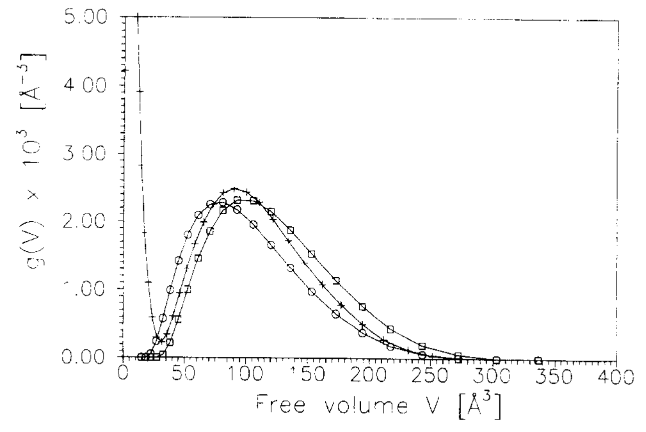

Figure 4 Free volume distribution $g(V)$ of polycarbonate (+, at 293 K) and tetramethylpolycarbonate (□, at 293 K; ○, at 112 K). The distributions are calculated according to equation (3) from data shown in *Figure 3*. Smooth curves are drawn through data points for clarity

Our present results, however, directly support the implications of a recent combined pVT, SAXS and WAXS study of TMPC and PC[21] that the mean free volume as well as the width of its distribution are not universal quantities for polymers in general; rather, they are closely related to the chemical structure of the polymers.

Table 2 summarizes the expansion coefficients of holes as well as the expansion coefficients of the bulk material obtained from dilatometric measurements[26]. The data for PC are also shown for comparison. *Table 2* makes it evident that the modified form of the PC exhibits a 2.5 times lower expansion coefficient of holes than PC, yet the macroscopic expansion coefficients are approximately equal. This implies that the thermal expansion in both materials is controlled by different mechanisms. The change of density of PC with temperature (thermal expansion) is dominantly due to the generation of the free volume caused by the occurrence of partial flips of the phenyl groups[9]. This mechanism is hindered in TMPC by the presence of the methyl groups attached to the phenyl ring. The difference observed in the behaviour of the annihilation and expansion characteristics is an indirect support of our microscopic model[9]. To summarize, it can be said that the mechanism of the volume expansion in TMPC takes place dominantly via the vibrational or librational degree of freedom; thus the generation of free volume in the form of holes is more difficult than in PC. The probable cause lies in the limited phenyl-flip dynamics of the substituted rings, which are considered as being the generators of the free volume in PC[9]. Recent n.m.r. experiments on TMPC support the substantially different dynamics of the phenyl groups after their quadruple substitution[27].

Our results in *Figures 1* and *2* show that not only τ_3 but also I_3 attain higher values in TMPC than in PC. This implies that the free volume fraction f_h is larger in TMPC than in PC. A method of extraction of the quantity f_h from the combination of dilatometric and positron annihilation measurements has been suggested in ref. 9. Unfortunately, this approach is not applicable to TMPC because of the absence of the macroscopic volume expansion data in the low temperature region. An alternative approach comes from the assumption that if the relative intensity I_3 is proportional to the number of holes, then it holds that the fractional free volume f_h is given as[8]:

Table 2 Thermal expansion coefficients determined from the dependencies of τ_3 and I_3 on T for TMPC and PC

Polymer	α_{τ_3} (K^{-1})	α_{I_3} (K^{-1})	$\alpha_{f_h}^{\mathrm{PAL}}$ (K^{-1})	α_f^{dil} (K^{-1})
PC[a]	1.07×10^{-3}	1.65×10^{-3}	2.1×10^{-3}	1.83×10^{-4} [b]
TMPC	4.4×10^{-4}	7.0×10^{-4}	8.4×10^{-4}	2.02×10^{-4} [b]

[a] From ref. 9

[b] From ref. 26

$$f_h(T) = C\tau_3(T)I_3(T) \tag{6}$$

Supposing that the coefficient C depends neither on the type of the polymer nor on the temperature, we have obtained $C = 0.41\ \mathrm{ns}^{-1}$ (ref. 9). The results of the calculations are given in *Table 3* together with the data for PC. The fourth column shows that the hole fraction f_h in TMPC is higher and increases with the temperature more slowly than in PC. This is again a consequence of a decreased packing tendency of the TMPC chains.

It is noteworthy to compare f_h determined from the o-Ps annihilation with the fractions of the so-called empty free volume, defined by the relation[28]:

$$f_e(T) = \frac{V(T) - V_W}{V(T)} \tag{7}$$

where $V(T)$ is the macroscopic volume of the polymer at the temperature T and V_W is the van der Waals volume of the polymer chains. This quantity represents the maximum possible free volume in a system at a given temperature with totally frozen motion. The results in *Table 3* [columns 5 (V_e) and 6 (f_e)] show a very weak and similar temperature dependence for both polymers, which is probably caused by the similar expansion coefficient of the bulk material. The value of f_e changes by about 7% during the change of temperature from 130 to 293 K. On the other hand, f_h changes substantially in the same temperature range; the changes being 52% for PC and 20% for TMPC. These facts again point to a different volume expansion mechanism of the investigated polymers.

From the values of f_h and f_e, we can roughly estimate the portion of the free volume inaccessible to o-Ps for either geometrical or dynamical reasons, i.e. of the volume of the free volume entities with radii below 1 Å or above 100 Å. This portion represents 61 and 42% at 130 K and 44 and 35% at 293 K for PC and TMPC, respectively. Considering that an effective free volume is always less than the empty one due to some motion, the above-mentioned values represent the upper limits only. In fact, the fraction of the free volume determined by

Table 3 Free volume fraction and concentration characteristics of PC and TMPC at three temperatures

Polymer	T (K)	V (cm^3 g^{-1})	V_h (Å^3)	f_h	V_e (cm^3 g^{-1})	f_e	$\bar{c}_h^m$ (hole g^{-1})	c_h^{mol} (hole mol^{-1})	c_h^{mon} (hole mol^{-1})	c_h^V (hole cm^{-3})	$v = 1/c_h^V$ (Å^3 hole^{-1})	l_h (Å hole^{-1})
PC[a]	130	0.805	76	0.126	0.259	0.322	1.34×10^{21}	3.39×10^{23}	0.56	1.66×10^{21}	608	8.5
	215	0.817	91	0.161	0.271	0.332	1.45×10^{21}	3.67×10^{23}	0.61	1.77×10^{21}	566	8.3
	300	0.833	109	0.193	0.287	0.345	1.48×10^{21}	3.75×10^{23}	0.62	1.78×10^{21}	565	8.3
TMPC[b]	130	0.894[c]	117	0.202	0.314	0.351	1.54×10^{21}	4.79×10^{23}	0.79	1.73×10^{21}	579	8.30
	215	0.910[c]	125.5	0.222	0.330	0.363	1.62×10^{21}	5.01×10^{23}	0.83	1.78×10^{21}	563	8.25
	300	0.926[c]	135	0.243	0.346	0.374	1.67×10^{21}	5.17×10^{23}	0.86	1.80×10^{21}	556	8.20

[a] From ref. 9

[b] This work

[c] Calculated using data from ref. 26

PAL will be somewhat higher. All these trends are reflections of a higher degree of defect, as well as of a lower level of internal mobility in TMPC as compared with PC.

The concentration aspect of the free volume characterization in both polycarbonates is shown in columns 7–10 in *Table 3*. The mass and molar representations of the mean hole concentration reflect a higher level of the free volume accessible to *o*-Ps in TMPC, as compared with PC. The consequence of this is the higher number of holes per monomer, c_h^{mon}. On the other hand, the volume concentrations of holes, c_h^V, are close to each other, which leads to similar geometrical characteristics such as the mean volume of the polymer per hole, or the mean distance between the neighbouring holes $\bar{l}_h$, assuming their homogeneous distribution in the matrix.

Free volume microstructures and various physical properties of PC and TMPC

The microstructural characterization of the polymers allows a quantitative discussion about the relationships between the free volume and the physical properties, as well as the correlation between the different physicochemical properties. So far, correlations have been based on the different operational definitions of the free volume, such as the empty volume, expansion volume and the fluctuation volume[28,29]. In the following section, some relationships are discussed between the free volume determined directly by the experimental PAL method and the mechanical and transport properties of both investigated polymers.

Relaxation behaviour. As the first example, we shall demonstrate the relaxation properties of PC and TMPC. It is known that both polymers exhibit pronounced γ-relaxation peaks at a frequency of 1 Hz around 173 and 323 K, respectively[30–34]. On the other hand, the bend in $\tau_3 - T$ dependence is observed around 130 K in PC[9]; no such effect is observed in TMPC at the measured temperature range. The connection between this bend and relaxation behaviour can be understood by considering the fact that the PALS method is characterized by two time scales; the first scale is connected with the *o*-Ps lifetime of several nanoseconds (a frequency of hundreds of MHz), and the other one is associated with a temperature–time regime of measurements. The latter scale is determined by a heating rate and can be estimated from temperature and time increments to be around 360 s (a frequency of 2.8×10^{-3} Hz). On this second scale, a certain structural reorganization of a matrix due to some slower motion can take place without detection. Then, using the bibliographic data for the activation energies of the γ-relaxations[30,34], we obtain for the expected temperatures of the γ-maxima $T_\gamma = 144$ K for PC and $T_\gamma = 276$ K for TMPC. In the case of PC, the proximity of the calculated value to the temperature of the bend (130 K) suggests a potential correlation of this bend with the occurrence of the γ-relaxation peak. In such a case, the γ-relaxation might be connected with the partial flip of the phenyl group. In recent works[32,35], a conclusion is made that, in spite of the accord of the frequencies of the γ-relaxation and the 180°-flip, the full flips do not participate in the γ-relaxation; thus the flips are more an indication rather than the cause of the γ-relaxation mode. But the quasistatic modelling of the chain dynamics in the bulk PC[36], which includes the phenyl flip motion and the conformational change of the carbonate group, suggests a two-barrier character of the complete phenyl rotation connected with the reorientation of the carbonate groups. Analogically, the rearrangement of the carbonate groups is coupled with the positional changes of the phenyl rings. It seems that the simultaneous occurrence of the γ-relaxation in mechanical and dielectric spectroscopies may be related with the above-mentioned relationship of the motion of the carbonate groups with the partial flips of the aromatic rings. This supposition is supported by the good agreement between the calculated typical barrier of the partial flip, $\sim$54 kJ mol^{-1}, and the experimental activation energies 42–54 kJ mol^{-1}, in bulk PC[34,35].

Fracture behaviour. The next field where the information from PAL is utilized is the macroscopic fracture behaviour of solid polymers, which are described in terms of the ductile–brittle material in the glassy state. High ductility of the PC down to low temperatures is well known[37]. On the other hand, TMPC is a brittle material even at room temperature[16]. Following the free volume concept, the high ductility could be related to the high level of structural disorder which would point to the increased mobility in the process of deformation[38,39]. According to this notion, however, the ductility behaviour in PC and TMPC should be opposite than that observed. Thus, the relatively high free volume is not a sufficient condition for the favourable deformation properties of the glassy polymers. Moreover, the mobility is not unambiguously determined by the free volume fraction in various polymer matrices.

An alternative hypothesis emphasizes the relationship between the ductility and the existence of the secondary relaxations[40,41]. A great difference in the ductility between TMPC and PC due to different localization of the corresponding γ-relaxations should be observed, but this relation is not of universal validity. Especially the annealing of the PC, i.e. the reduction of the free volume, has little influence on the γ-relaxation, although the polymer becomes more brittle[42]. This indicates a rather large scale nature of the ductility. Recent molecular modelling of the plastic response of bulk PC suggests a cooperative motion of many chain segments in the single plastic relaxation event[43]. Low temperature stress–strain measurements on PC exhibit the brittle–ductile transition at temperatures between 110 and 159 K (ref. 37). This transition correlates with the bend region about 130 K on our $\tau_3 - T$ dependence for PC[9]. It means that the change in the deformation regime is connected with the dynamic generation of new holes due to the course of partial flips of phenyl groups. Thus, this thermal generation of free volume entities enables cooperative rearrangements coupled with the large strain deformation. In the case of TMPC, a relatively small change in the free volume characteristics due to the hindered internal mobility is observed. This results in less favourable conditions for large scale deformation, in spite of the higher total free volume content. Our PAL observation suggests that probably both factors, i.e. the relatively high free volume content as well as the high internal flexibility of the parts of the chains, are necessary conditions for the favourable deformation properties of the polymer glasses in a wide temperature interval.

Gas transport behaviour. Another physical property which is correlated with the free volume is the gas transport in polymers. Several studies of the sorption and diffusion of different penetrants in PC and TMPC have already been performed[26,33,44]. Different permeability coefficients P and solubility coefficients S, as well as diffusion coefficients D, have been observed—see *Table 6* in ref. 26. These differences can be discussed in the light of the free volume information obtained by PAL measurements.

The solubility coefficients S, as thermodynamic terms of permeability, depend on the condensibility of the penetrant, on the interaction between the penetrant and the polymer and, in the case of glassy polymers, on the magnitude of the non-equilibrium free volume holes in the matrix[26,44]. Gas sorption isotherms in glassy polymers are generally well described by the dual sorption model.

$$c = c_{\mathrm{D}} + c_{\mathrm{H}} = k_{\mathrm{D}} \cdot p + \frac{c'_{\mathrm{H}} \cdot b}{1 + bp} \cdot p$$

The first term represents a Henry's mode of sorption, as found in liquids and rubbery polymers, and the second term is a Langmuir mode of sorption which is believed to originate from the non-equilibrium nature of the glassy state. The parameter k_{D} is the Henry law solubility coefficient, c'_{H} is the Langmuir sorption capacity and b is affinity parameter. The ratios of solubility coefficients for a series of gases He, O_2, N_2, CH_4 and CO_2 are 1.7, 2.6, 3.0, 1.8 and 1.5, respectively, as shown in Table 6 of ref. 26. The same is valid for the ratios of the Langmuir sorption capacity (Table 2 of ref. 26). The ratios of Henry's solubilities fall into a relatively narrow range (1.1–1.6). It follows from our results that the mean number of holes per mole, $\bar{c}_{\mathrm{h}}^{\mathrm{mol}}$, is significantly higher in TMPC and attains 1.4 times the value in PC at 293 K. This suggests that the solubility of gases ought to be higher in TMPC in gross qualitative agreement with the above mentioned solubility ratios. In view of the fact that the kinetic diameters of gases are different and that *o*-Ps detects only a certain fraction of the total free volume accessible due to geometrical and/or dynamical reasons, the qualitative estimate is good, although other factors, such as an enhanced interaction between penetrant and matrix with the substitution in the case of k_{D} (ref. 26), and different sample histories also play their role.

On the other hand, let us consider the diffusion of the penetrant molecule in the polymer matrix as a jumping process over a mean distance λ from one site to another free hole. The diffusion coefficient D as a kinetic term of the permeability process depends on the inter-segmental packing density and on the internal mobility of the polymer[44]. Then, according to Meares's diffusion model[45], the mean distance λ can be estimated from the experimental activation energy E_{d} using the relationship:

$$E_{\mathrm{d}} = (\pi/4)d^2\lambda CED$$

where d is the kinetic radius of the penetrant and CED is the cohesive energy density. *Table 4* shows the results of calculations of λ from the experimental values of the diffusion of O_2 and N_2 in both PC and TMPC. In spite of the fact that the estimated values of λ are larger than the mean distances between the holes $\bar{l}_{\mathrm{h}}$ obtained from the free volume PAL analysis, their proximity for both polymers is interesting, similar to that of the $\bar{l}_{\mathrm{h}}$ values seen in *Table 3*. Lower values of $\bar{l}_{\mathrm{h}}$ are related to the relatively strong assumption about the homogeneous distribution of the holes in the matrix. In reality, *Figures 3* and *4* can be understood as a certain 'clustering' of the holes, which leads to the effective increase of the distance between the neighbouring free volume entities. These estimates indicate the hopping model of the diffusion as a very probable mechanism of transport of the gas penetrants in the polymer glasses. Recent molecular simulations of this process support such physical pictures of the gas transport in a glassy polymer[46,47]. Moreover, one of these molecular simulations of the diffusion of small penetrants in PC[47] indicates an existence of channels between diffusion sites. The lengths of such channels are around 10 Å, which is in accordance with our estimates.

Table 4 Results of fitting of Meares' model on diffusion data of O_2 and N_2 in PC and TMPC

		d^b (Å)		E_{d}^{c} (kJ mol^{-1})		λ (Å)	
Polymer	CED^a (cal Å^{-3})	O_2	N_2	O_2	N_2	O_2	N_2
PC	88.2×10^{-24}	3.64	3.80	30.0	35.6	13.0	14.0
TMPC	74.5×10^{-24}	3.64	3.80	26.9	28.8	13.7	13.6

[a] Calculated using Small's group contribution method[48]
[b] From ref. 13
[c] From ref. 26

We should understand, however, that although the solubility as well as the diffusion may depend on the free volume, and even may depend principally on the free volume, it does not depend exclusively on the free volume characteristics.

CONCLUSIONS

The results of the PAL measurements on amorphous tetramethylpolycarbonate are presented. Temperature dependencies of the mean lifetime of the *o*-Ps and of the relative intensity are interpreted in free volume terms as the mean size of the free volume entity and the concentration of these entities in different representations. A comparison with a similar study performed on PC[9] yields that TMPC has higher free volume content, realized through the higher number of larger free volume entities. The molecular cause of these differences is the quadruple methylation of the aromatic rings leading to a less effective packing of the chains, as well as to a decrease in the flip dynamics of the phenyl rings. Finally, the influence of the different free volume microstructures on the relaxation and fracture behaviours as well as on the penetration of TMPC and PC by gases, is discussed.

ACKNOWLEDGEMENTS

The authors express their thanks to Dr G. Hellmann from Deutsches Kunststoff Institut, Darmstadt, Germany, for kindly providing the material, and to the Grant Agency for Science of the Slovak Republic for the support of this research (grant No. 2/55/93). The work has been partially funded by the International Atomic Energy Agency (contract No. 6476/R1/RB).

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