

Anisotropy of free-volume-hole dimensions in polymers probed by positron-annihilation spectroscopy

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The structures of atomic-scale free-volume holes in stretched [poly(aryl-ether-ether-ketone)] PEEK and [poly(methyl methacrylate)] PMMA polymers were determined as a function of orientation by measuring the angular correlation of annihilation radiation from parapositronium trapped in the holes. The measured average hole diameters were found to range from 0.80 ± 0.03 to 0.31 ± 0.02 nm and from 0.70 ± 0.03 to 0.42 ± 0.02 nm, depending on orientation, in stretched PEEK and PMMA, respectively. Thus, the free-volume holes were ellipsoids with anisotropies of 2.6 ± 0.2 and 1.7 ± 0.2 for PEEK and PMMA, respectively.

The utilization of polymers in industrial applications requires a basic understanding of their material properties. A key problem in this regard is relating the macroscopic mechanical properties (e.g., impact strengths, moduli) of polymers to atomic-scale free-volume holes ranging in diameter from tenths of a nanometer to a few nanometers.¹ In spite of a great deal of research effort expended in the past decades to understand the physical properties of free volume, only limited information about hole size, concentration, and shape has been forthcoming.

Conventional experimental techniques potentially relevant to this line of investigation are small-angle diffraction methods,² and photochromic and fluorescence spectroscopies,³ which give an estimate of the mean free-volume-hole size. However, the diffraction methods become very difficult for hole sizes below 1 nm because of the intrinsic limitations of the methods, in which the hole sizes are reduced indirectly from the bulk parameters. From our best knowledge, no information on hole sizes below 1 nm in polymers has been reported by the diffraction methods. And photochromic and fluorescence spectroscopies require the introduction of probe molecules with sizes comparable to the hole sizes, so that the extracted information about atomic-scale free volume is only indirect.

A technique that provides a direct means of measuring atomic-scale free-volume-hole size is positron-annihilation lifetime spectroscopy (PAL).⁴ However, this technique is capable of measuring only mean hole size and not hole shape.

In this paper we report direct measurements of the shapes of atomic-scale free-volume holes in two oriented polymers, i.e., PEEK [poly(aryl-ether-ether-ketone)] and PMMA [poly(methylmethacrylate)], in which we measured the angular correlation of positron-annihilation radiation (ACAR).

Amorphous PEEK (from Imperial Chemical Inc. Americas) has a glass-transition temperature T_g of

144 °C. This 98+ % amorphous PEEK was prepared by rapid quenching from the melt and has a density of 1.264×10^3 kg/m³.⁵ The amorphous PEEK sample examined by ACAR was first stretched uniaxially at room temperature and then allowed to relax. The final ratio of the stretch axis to the narrow axis was 2.60. The lightly cross-linked PMMA samples ($T_g = 120$ °C) were cut from a DC-8-aircraft (McDonnell Douglas) cabin window. The as-received samples had been stretched equally, above T_g , in two-dimensions, with a measured in-plane to out-of-plane stretch ratio of 4.43.

The positron-annihilation experiments were performed by collecting ACAR data as a function of sample orientation at room temperature. The positron source was 3-mCi ²²NaC₂H₃O₂ deposited in a thin aluminum-foil envelope (Al thickness, 4 μm; range, 1.1 mg/cm²), with a 1-mm-diam active region. It was inserted between two identical sample halves.

The one-dimensional (1D) ACAR spectrometer had the following configuration: The distance between the sample and the Na(I) detectors was 6.6 m, the dimensions of the detector openings (slits) were 60 (height) × 0.5 cm² (width). The moving detector was driven by a stepping motor (4000 steps/in.) GPIB (General Purpose Interface Board) interfaced with an IBM PS-2 computer. Angular displacement of the moving detector was measured relative to the direction of colinearity with the sample and fixed detector. The ACAR spectra were recorded as coincident counts (time window, 100 ns) between the fixed detector and the moving detector versus angular deviation (up to 60 mrad) from colinearity (zero transverse momentum). The angular resolution of spectrometer was 1.10 mrad, as determined from the full width at half maximum (FWHM) of the narrow ACAR component of an oriented quartz sample. Each ACAR spectrum contained about 5×10^5 counts, recorded over a period of 3 days.

For PEEK, the sample orientation was measured as

the angle between the unique stretch direction and the direction of travel of the movable detector. For PMMA, the sample orientation was measured as the angle between a vector lying in the stretch plane and the direction of detector travel. Thus, for both samples, 0° and 90° correspond to the stretch direction(s) and the narrow direction(s), respectively, being oriented in the direction of detector travel.

The experimental spectra were fitted with a sum of Gaussian distributions using the computer program PATFIT.⁶ All spectra were initially fitted with two to five Gaussians; the three-Gaussian fits gave the most consistent and stable results with a χ^2 of less than 1.5. We therefore report three-Gaussian results.

The area normalized ACAR spectra for two extreme orientations of the stretched PEEK sample are shown in Fig. 1. Overall, the ACAR spectrum appears narrower for the 0° orientation than the 90° orientation. Although the spectra were obtained in the angles ± 60 mrad, we only plotted the data in the regions ± 8 mrad, where significant differences are observed at two orientations, in Fig. 1. Widths for other orientations lie between the values at these two extremes. Similar results were obtained from the PMMA samples. The parameters obtained from fitting the data are summarized in Table I.

In order to extract free-volume-hole dimensions from the fit parameters (the FWHM and intensities) of the ACAR spectra one must consider all the possible positron and positronium states that contribute to the observed spectra. When a positron is injected into a polymeric material, it can annihilate with an electron directly or it can pick up an electron and form a bound-state positronium, Ps. In a systematic study of positron annihilation lifetime as a function of degree of crystallinity in semicrystalline PEEK samples,⁵ we found that Ps was formed and annihilated only in the amorphous regions, where free-volume holes were present. No Ps annihilation was observed from the crystalline regions, which

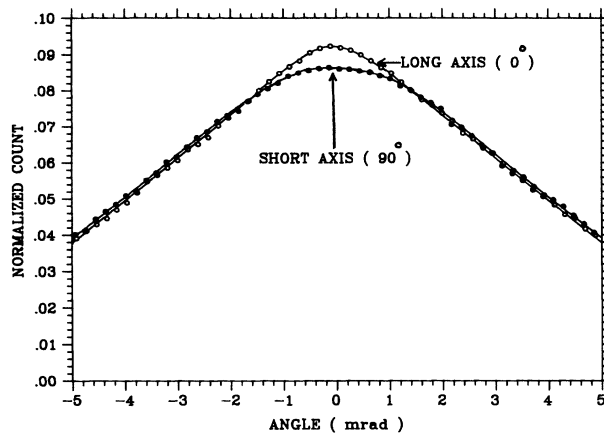


FIG. 1. ACAR spectra from stretched PEEK at two orientations. 0° (open circles) and 90° (solid circles) correspond to the stretch (long) direction and the narrowed (short) direction, respectively, being oriented in the direction of detector travel. The spectra were normalized to the total counts of each spectrum within the experimental angles, ± 60 mrad. The lines are the fitted three-Gaussian functions.

contained only bulk matrix. Consequently, we concluded that positron-annihilation radiation arises solely from positrons and Ps in free-volume holes, which act as effective trapping sites for positron and Ps. Such localized positrons or Ps may also form bound molecular states with the polymer. We therefore identify the following four states that could possibly contribute to the ACAR spectra: positrons in free-volume holes, orthopositronium (*o*-Ps; triplet) in free-volume holes, parapositronium (*p*-Ps; singlet) in free-volume holes, and positron or Ps-molecular bound states.

In molecular (i.e., nonionic, nonmetallic) substrates, *o*-

TABLE I. ACAR results.

Samples	Orientation (deg)	FWHM ₃ ^{a,b} (mrad)	FWHM ₂ ^{a,b} (mrad)	FWHM ₁ ^{a,b} (mrad)	Free-volume ^c diameter (nm)
Stretched PEEK	0°	18.8	8.1	2.94	0.797 ± 0.030
Stretched PEEK	23°	16.4	6.7	4.13	0.472 ± 0.029
Stretched PEEK	45°	16.7	7.0	4.28	0.444 ± 0.027
Stretched PEEK	68°	15.5	7.2	4.70	0.374 ± 0.021
Stretched PEEK	90°	17.2	6.0	5.19	0.308 ± 0.020
Unstretched PEEK		16.8	6.3	3.92	0.515 ± 0.029
PMMA	0°	18.3	8.2	3.20	0.706 ± 0.029
PMMA	23°	17.9	9.7	4.13	0.472 ± 0.020
PMMA	45°	16.7	9.6	4.30	0.440 ± 0.020
PMMA	90°	17.0	10.0	4.42	0.419 ± 0.019

^aThe standard deviations for FWHM₃, FWHM₂, and FWHM₁ are 0.02–0.3, 0.5–0.6, and 0.7 mrad, respectively.

^bThe intensities for FWHM₃, FWHM₂, and FWHM₁ are 5–7%, 86–88%, and 7.30% (unstretched) or 6.70% (stretched) for PEEK, and 4–5%, 86–87%, and 8.96% for PMMA, respectively. The intensities of FWHM₁ components (% of *p*-Ps) were fixed at the $\frac{1}{3}$ values of I_3 (% of *o*-Ps) as obtained by the lifetime measurements (listed in Table II).

^cFree-volume diameters were calculated from Eq. (1) and by using FWHM₁ as $\theta_{1/2}$.

Ps undergoes a pick-off annihilation with electrons having different momenta; therefore, *o*-Ps contributes to the broadest ACAR component, having a FWHM of 17 mrad and a relative intensity of 4–7%. This intensity is less than the value observed by the PAL technique (20–26%) because the ACAR data were collected only to an angle of 60 mrad, whereas in the PAL technique the data correspond to all ACAR angles. The intermediate width component, with a FWHM of 6–10 mrad and a relative intensity of ~87%, is assigned to the annihilation of positrons and positron-molecular species.

The narrow component, with a FWHM varying from 2 to 5 mrad, is easily identified as being from *p*-Ps localized in free-volume holes. The intensity of this component ranges from 5% to 9% in an unconstrained data analysis. Since these intensities are very close to the theoretical one-third of the *o*-Ps intensities (PAL experiments give *o*-Ps intensities of 20.1% and 26.7% for PEEK and PMMA, respectively), we fix the intensities of the narrow ACAR components at exactly one-third of these *o*-Ps values, i.e., 6.7% and 8.9% for PEEK and PMMA, respectively. The FWHM results shown in Table I, which were obtained using these constraints, give as good χ^2 values as obtained for unconstrained fits. The narrowed components vary systematically as a function of orientation from 2.9 ± 0.1 to 5.2 ± 0.1 mrad for PEEK, and from 3.2 ± 0.1 to 4.4 ± 0.1 mrad for PMMA.

From the FWHM of the narrow component, FWHM1, we can determine the dimensions of the free-volume holes in PEEK and PMMA. In order to obtain these dimensions from the ACAR spectra, we use a simple model for the quantum particle *p*-Ps in a finite hole: We assume a hole of diameter L bounded by an infinite potential. On the inside surface of the hole is an electron layer of uniform density and thickness ΔL . This model was originally suggested by Tao⁷ and Eldrup, Lightbody, and Sherwood.⁸

We obtain a semiempirical equation between the experimental FWHM1 ($\theta_{1/2}$), which is a result of the zero-

point vibrational motion of *p*-Ps, and any finite hole diameter (L):⁹

$$L = 3.32/\theta_{1/2} - 0.332, \quad (1)$$

where L and $\theta_{1/2}$ are expressed in the units of nm and mrad, respectively. The last term of Eq. (1) is the thickness of the electron layer, which is determined semiempirically using a relation between bubble size and observed *o*-Ps lifetime in liquids.⁹ From the measured values of $\theta_{1/2}$ we calculate the diameters of the free-volume holes according to Eq. (1) and the results are listed in Table I. These hole diameters are plotted as a function of orientation for PEEK and PMMA in Figs. 2 and 3, respectively. The sizes of the holes range from 0.31 ± 0.02 to 0.80 ± 0.03 nm in the PEEK sample and from 0.42 ± 0.02 to 0.70 ± 0.03 nm in the PMMA sample. It is worthwhile to mention that the obtained hole sizes are the mean values of the actual hole sizes which are distributed in a certain function. In principle, ACAR spectra contain such information of size distribution. The development of resolving such distribution is a mathematically complicated problem which is currently in progress at our laboratory.

The mean hole sizes can also be determined using the PAL technique.^{9–11} In a quantum model similar to that employed for ACAR, we obtained a relationship between hole diameter (L) and *o*-Ps lifetime (τ),⁹

$$1/\tau = 2\{1 - L/(0.332 + L) + \sin[2\pi L/(0.332 + L)]/2\pi\}, \quad (2)$$

where τ and L are expressed in the units of ns and nm, respectively.

Lifetimes obtained from PAL experiments conducted on the identical PEEK and PMMA samples as used in the ACAR experiments are listed in Table II. Values for L calculated using Eq. (2) are also listed and are in good agreement with the values of L in Table I. Thus, in these

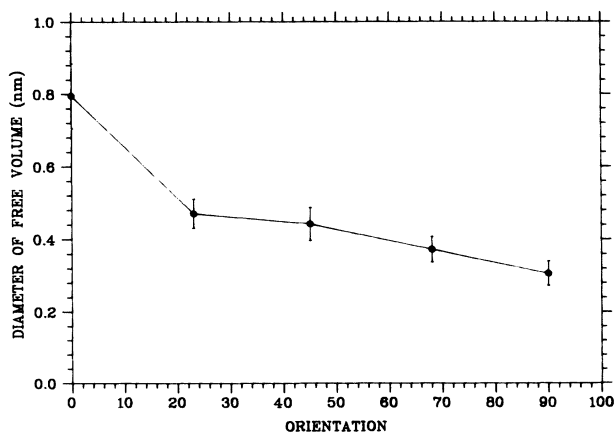


FIG. 2. Free-volume-hole diameter vs angle of rotation in uniaxially stretched PEEK samples. 0° and 90° refer to the stretch direction and the narrowed direction, respectively, being oriented in the direction of detector travel.

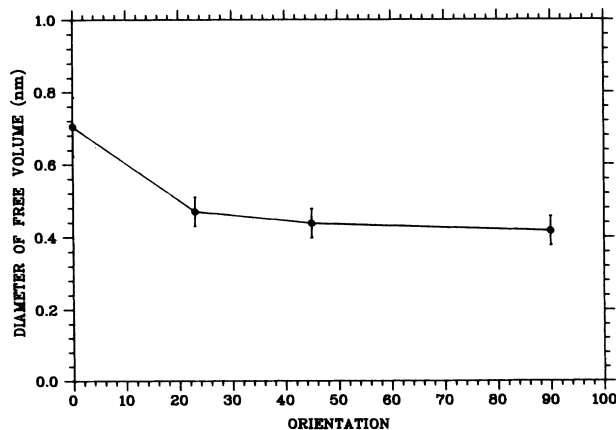


FIG. 3. Free-volume-hole diameter vs angle of rotation in two-dimensionally stretched PMMA samples. 0° and 90° refer to the stretch direction and the narrowed direction, respectively, being oriented in the direction of detector travel.

TABLE II. Positron lifetime results.

Sample	τ_1 (ns) ^a	τ_2 (ns) ^d	τ_3 (ns) ^a	I_3 (%) ^b	Free-volume ^c diameter (nm)
PEEK (stretched)	0.161	0.436	1.785	20.09 ^d	0.530±0.019
PEEK (unstretched)	0.210	0.458	1.751	21.91	0.522±0.020
PMMA (stretched)	0.150	0.395	1.873	26.88	0.549±0.021

^aThe standard deviations for τ_1 , τ_2 , τ_3 , and I_3 are 0.007 ns, 0.016 ns, 0.012 ns, and 0.13%, respectively.

^bThe I_1 and I_2 are 12–26 % and 45–54 %, respectively.

^cThe free-volume diameters are calculated from Eq. (2) using τ_3 data.

^dA slightly smaller value of I_3 for the stretched PEEK as compared to that of the unstretched samples is due to an increase of crystallinity of stretching the PEEK samples.

oriented samples, the diameters determined from lifetime data are closer to the mean values of those determined from ACAR at different orientations. The experimental accuracies of the diameters are estimated to be about 10% for both the lifetime and ACAR methods.

From the ratio of the free-volume-hole diameters at 0° and at 90°, the calculated hole anisotropies are 2.6 ± 0.2 and 1.7 ± 0.2 for the PEEK and PMMA samples, respectively. Therefore, the free-volume holes in the 1D-stretched PEEK are approximated as prolate ellipsoids, whereas in the 2D-stretched PMMA they are oblate ellipsoids. The obtained hole anisotropies compare with the macroscopic stretched ratios favorably for the case of PEEK, but less favorably for the case of PMMA. We be-

lieve this is because the PEEK samples were stretched below T_g and the PMMA samples were stretched above T_g .

In summary, we report direct measurement of the orientation-dependent dimensions of free-volume holes in two stretched polymers obtained using ACAR spectroscopy. ACAR has been shown to be a unique technique for characterizing the structure of such free-volume holes.

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