

FINAL
IN 27-CR
027485

Final Report

6 CIT
1 REF.

Submitted to:

National Aeronautics and
Space Administration,
Langley Research Center,
Hampton, VA 23665-5225
Attn: Dr. Jag J. Singh
Technical Office, M/S 235

11P.
275358

Institution:

Hampton University,
Department of Physics,
Hampton, VA 23668

Title of Research:

Investigation of Polymer liquid
Crystals

NASA Grant No:

NAG-1-1168

Period Covered:

October 1, 1990 - Sept 30, 1996

Principal Investigator:

Dr. Kwang S. Han

Final Report

Submitted to: National Aeronautics and
Space Administration,
Langley Research Center,
Hampton, VA 23665-5225
Attn: Dr. Jag J. Singh
Technical Office, M/S 235

Institution: Hampton University,
Department of Physics,
Hampton, VA 23668

Title of Research: Investigation of Polymer liquid
Crystals

NASA Grant No: NAG-1-1168

Period Covered: October 1, 1990 - Sept 30, 1996

Principal Investigator: Dr. Kwang S. Han

Table of Contents

I.	Summary	1
II.	Introduction	1
	1. Free volume model for molecular weights of polymers	1
	2. Free volume in glassy poly (Arlene Esther Ketone's)	2
	3. Free volume characteristics of epoxies	2
	4. Low energy positron flux generator for microstructural characterization of thin films	2
	5. Microstructural characterization of thin polyamide Films by Positron Lifetime Spectroscopy	3
	6. Positron lifetime spectroscopy for investigation of thin polymer coatings	4
	7. Semi-Interpenetrating polymer networks	5
III.	References	5
IV.	List of publication and conference papers generated under NAG1-1168	6
V.	List of scientific personnel participated under NAG1-1168	8
VI.	List of Appendix	8

PRIMARY
IN-27
027485

I. Summary

The positron annihilation lifetime spectroscopy (PALS) using a low energy flux generator may provide a reasonably accurate technique for measuring molecular weights of linear polymers and characterization of thin polyimide films in terms of their dielectric constants and hydrophobity etc. Among the tested samples are glassy poly arylene Ether Ketone films, epoxy and other polyimide films. One of the proposed technique relates the free volume cell size (V_f) with sample molecular weight (M) in a manner remarkably similar to that obtained by Mark Houwink (M-H) between the inherent viscosity (η) and molecular weight of polymer solution. The PALS has also demonstrated that free-volume cell size in thermoset is a versatile, useful parameter that relates directly to the polymer segmental molecular weight, the cross-link density, and the coefficient of thermal expansion. Thus, a determination of free volume cell size provides a viable basis for complete microstructural characterization of thermoset polyimides and also gives direct information about the cross-link density and coefficient of expansion of the test samples. Seven areas of the researches conducted are reported here.

II. Introduction

The work performed during the period from Oct 1, 1990 to Sept 30, 1996 under NASA grant (NAG1-1168) were mainly microstructural characterization of polymeric materials, using a low energy positron flux generator and conventional positron spectroscopy. Among many tasks performed at PALS of Langley Research Center, we report here the following categories.

1. Free volume model for molecular weights of polymers - TITLE

A free volume model has been developed for determining molecular weights of linear polymers. It is based on the size of free volume cells in two geometries poly (arylene ether ketone)s. Free volume cell sizes in test sample were measured using positron lifetime spectroscopy. The molecular weights computed from cell sizes are in good agreement with the values measured by gel permeation chromatography, with a low angle laser light scattering photometer as the detector. The model has been further tested on two atactic polystyrene samples, where it predicted the ratio of their molecular weights with reasonable accuracy. Details of experiments and results are described in Ref. 1, 2 and appendix 1 and 2, respectively.

2. Free volume characteristics of glassy poly (arylene Ether Ketone)

Amorphous poly arylene ether ketones were examined in the glassy state by Positron Annihilation Lifetime Spectroscopy (PALS) and in the melt by standard rheological techniques. Specimens were well-characterized fractions of two isomeric structures. PALS clearly shows the polymer with meta linkages in the backbone contains large voids (>0.25 nm radius). Thus despite their similar bulk densities, the two materials must pack very differently on a local scale. On the other hand, free volumes inferred from the WLF treatment of melt viscosity data are practically identical in both materials ca. 4% at glass transition temperature (T_g). The comparison between techniques sheds some light on the distribution of free volume. Details of experiments and results are described in Ref. 3 and appendix 3.

3. Free Volume Characteristics of Epoxies

Positron annihilation spectroscopy has been used to measure free-volume characteristics of selected epoxies. Fluorene resins, a new family of high temperature thermosetting resins, were selected as the test medium. Experimental results indicate that the free-volume cell size V_f varies with the molecular weight between the cross-linked M_c according to an equation of the form $V_f = AMB_c$ where A and B are structure constant. In two of the samples, the concentration of bulky fluorene groups was increased in the network backbone by replacement of some of the conventional bisphenol A epoxy resin with the fluorene-derived epoxy resin. This resulted in an increase in their glassy transition temperature for a given level of cross-linking. It has been found that, in these samples, the Doppler broadening of the annihilation peak decreases with the increasing fluorene content, presumably due to enhanced damping of the chain motions. Details of experiments and results are described in Ref. 4 and appendix 4.

4. Low Energy Positron Flux Generator for Microstructural Characterization of Thin Films

A slow positron flux generator using well-annealed polycrystalline tungsten moderators and a ^{22}Na positron source has been developed for life time studies in thin polymer films. A $250 \mu\text{C}$ source, deposited on a $2.54 \mu\text{m}$ thick aluminized mylar film, is sandwiched between two 0.0127 cm thick 2.54×2.54 cm tungsten strips. Two 2.54 cm by 2.54 cm test polymer films, whose thickness ranges from 0.00127 to 0.0127 cm, insulate the two tungsten moderator strips from the

aluminized mylar source holder. A potential difference of 10-100 V, depending on the test polymer film thickness, is applied between the tungsten strips and the source holder. Thermalized positrons diffusing out of the moderator strips are attracted to the source holder when it is at a negative potential. On the other hand, they are prevented from entering the test polymer films when the source holder is at a positive potential. The difference between the positron lifetime spectrum with source at $\pm V$ is strongly related to the test film spectrum. Details of experimental technique and results are described in Ref. 5 and Appendix 5.

5. Microstructural characterization of thin polyimide films by Positron Lifetime Spectroscopy

Positron lifetime have been measured in series of thin aromatic polyimide films for microstructural characterization. No evidence of positronium formation was observed in any of the films investigated. All tests films exhibited only two positron lifetime components, the longer component corresponding to the positron annihilating at shallow traps. Based on these positron lifetimes, free volume fractions have been calculated for all the films tested. The free volume model has been developed to calculate the dielectric constants of thin polyimide films. The experimental and the calculated values for the dielectric constants of the films tested are in reasonably good agreement. It has been further noted that the presence of bulky CF_3 groups and meta linkages in the polyimide structure results in the higher free volume fraction and, consequently, lower dielectric constant values for the films studied. Details of experimental technique and results are described in Ref. 6 and appendix 6.

6. Positron Lifetime Spectroscopy for Investigation of thin Polymer Coatings

In the aerospace industry, applications for polymer coatings are increasing. They are now used for thermal control on aerospace structures and for protective insulating layers on optical and microelectronic components. However, the effectiveness of polymer coatings depends strongly on their microstructure and adhesion to the substrate. Currently no technique exists to adequately monitor the quality of these coatings. We have adapted positron lifetime spectroscopy to investigate the quality of thin coatings. Results of measurements on thin (25- μm) polyurethane coatings on aluminum and steels have compared with measurements on thicker (0.2-cm) self-standing polyurethane discs. We find the positron lifetime groups centered around 560 psec, which corresponds to the presence of 0.9- A^3 free volume cells. However, the number of these free-volume cells in thin coating is larger than in thick discs. This suggests that some of these cells

may be located in the interfacial regions between the coatings and the substrates. These results and their structural implications are described in Ref. 7 and Appendix 7.

7. Semi-Interpenetrating polymer networks

Thermoset and thermoplastic polyimides have complementary physical/mechanical properties. Whereas thermoset polyimides are brittle and generally easier to process, thermoplastic polyimides are strong but harder to process. It is hoped that a combination of these two types of polyimides may help produce polymers more suitable for aerospace applications.

Semi-Interpenetrating polymer networks (S-IPN) of thermoset LARCTM RP-46 and thermoplastics LARCTM IA polyimides were prepared in weight percent ratios ranging from 100:0 to 0:100. Positron lifetime measurements were made in these samples to correct their free volume features with physical/mechanical properties. As expected, positronium atoms are not formed in these samples. The second lifetime component has been used to infer the positron trap dimensions. The free volume goes through a minimum at about 50:50 ratio, suggesting that S-IPN samples are not merely solid solutions of the two polymer. Details of experiments and the related result are described in Ref. 8

III. References

1. "Free volume model for molecular weights of polymers", J. J. Singh and A. Eftekhari, Nuclear Instruments and Methods in Physics Research B63 477-483 (1992) .
2. "Free volume variation with molecular weight of Polymers " J. J . Singh, Abe Eftekhari, Jeffrey A Hinkley, Terry L. St. Clair, and Brian J. Jenson, NASA Tech. Memo. 4326 Feb (1992).
3. "Free Volume in Glassy Poly(arylene ether ketone)s", J. A. Hinkley, A. Eftekhari, R. A. Cook, B. J. Jensen and J. J. Singh, J. Poly. Sci-Poly. Vol. 30, pp. 1195-1198, 1992.
4. "Free Volume Characteristics of Epoxies ", Jag. J. Singh, Abe Eftekhari, William J. Schultz and Terry L. St. Clair, NASA Tech. Memo 4390. Sept (1992).
5. "Low Energy Positron Flux Generator for Microstructural Characterization of Thin Films", J.J.Singh, A. Eftekhari and T. L. St. Clair, Material Science Forum Vols. 105-110, pp1985-1988 (1992).
6. "Microstructural Characterization of Thin Polymer Films by Positron Lifetime Spectroscopy", A. Eftekhari, A. K. St. Clair, D. M. Stoakley, Danny R. Sprinkly and J. J. Singh, ACS. Symposium Series 537, Ch38 536-545 (1994)
7. "Positron Lifetime Spectroscopy in Thin Polymer Coatings" J. J. Singh, Abe Eftekhari, and Danny R. Sprinkle, NASA TM 4421 Feb. (1993).
8. "A Method for Characterizing Thermoset Polyimides " C. Ranganathaiah, D. R. Sprinkle, R. H. Pater and A. Eftekhari, NASA Tech. Memo 4707, March 1996.

IV. List of publications and conference papers
generated
under NASA Grant No. NAG1-1168
Period Oct 1, 1990 - Sept 30, 1996

1. "A Shear Sensitive Monomer Liquid Crystal System" J. J. Singh, **Abe Eftekhari** and D. S. Parmer, BAPS 36, 448 (1991).
2. "Positron Lifetime Measurements in Mixture of Chiral Nematic Liquid Crystals", J. J. Singh, **Abe Eftekhari**, and D. S. Parmer, NASA TP-3122, May 1991.
3. "Free Volume in Glassy Poly (Arlene Ether ketone)s", J. A. Hinkley, **Abe Eftekhari**, R. A. Cook, B. J. Jensen and J. J. Singh, J. Poly. Sci-Poly. Vol. 30, pp. 1195-1198, 1992.
4. "Free Volume Variation with Molecular Weight of Polymers""", J. J. Singh, **Abe Eftekhari** and T. L. ST Clair, & William J. Schultz, NASA Technical Memo. 4326 Feb. (1992).
5. "Free Volume in Glassy Poly Arlene Ethers", J. A. Hinkley, **Abe Eftekhari**, R. A. Crook, B. J. Jensen, and J. J. Singh. Journal of Polymer Sciences: Pat B: Polymer Physics, Vol. 30, 1195-1198 (1992).
6. "Free Volume Model for Molecular Weights of Polymer", J. J. Singh and **Abe Eftekhari**, Nuclear-Instruments and Methods in Physics Research-B Vol. 63 477-483 (1992).
7. "A Low-Energy Positron Flux Generator for Annihilation Studies", J. J. Singh, **Abe Eftekhari**, T. L. St Clair, Material Science Forum Vol. 105, 110 (1992).
8. "Free Volume Characteristics of Epoxies ", J. J. Singh, **Abe Eftekhari**, William J. Schultz and Terry L. St. Clair, NASA Tech. Memo 4390. Sept (1992).
9. "Positron Lifetime Spectroscopy in Thin Polymer Coatings"" J. J. Singh, **Abe Eftekhari**, and Danny R. Sprinkle, NASA TM 4421 Feb. (1993).
10. "Free Volume Model for Dielectric Constant of Polymer Films" **Abe Eftekhari**, Anne St. Clair, Diane M. Stockly, Danny R. Sprinkle, and J. J. Singh, 5th International Conf. on Slow Positron Beam Technique for Solids and Surfaces, Jackson Hole, Wyoming, Aug 1992.
11. "Microstructural Characterization of Thin Polymer Films using Langley Low Energy Positron Flux Generator" J. J. Singh, **Abe Eftekhari**, and Terry L. St. Clair, 12th International Conf. on Application of Accelerators in Research & Industry", Denton, Texas, Nov, (1992).
12. "Microstructural Characterization of Thin Polymer Films by Positron Lifetime Spectroscopy", **Abe Eftekhari**, A. K. St. Clair, D. M. Stoakley,

- Danny R. Sprinkly and J. J. Singh, ACS. Symposium Series 537, Ch38 536-545 (1994).
13. "Morphological Studies of Liquid Crystals by Positron Spectroscopy", J. J. Singh, Abe Eftekhari, and D. S. Parmer, at University of Texas at Arlington, Texas Nov (1992).
 14. "Investigation of Oxygen-induced quenching of phosphorescence in photo-excited molecules for the pressure sensitive paints" 13th Int. Conf. on the Application of Accelerators in Research and Industry. (1994).
 15. "Microstructural Characterization of Semi-Interpenetrating Polymer Networks by Positron Lifetime Spectroscopy" Abe Eftekhari, Ruth H. Pater and Jag J. Singh, ACS. Nuclear Chemistry and Technology Positron Muon Symposium (1996).
 16. "A Method for Characterizing Thermoset Polyimides " C. Ranganathaiah, D. R. Sprinkle, R. H. Pater and Abe Eftekhari, NASA Tech. Memo 4707, March 1996.

List of Student's Publication
generated
under NASA Grant No. NAG1-1168
Period Oct 1, 1990 - Sept 30, 1996

"Ionized-Cluster Beam Deposition of Phthalocyanine and a Microvoid Characteristic Study using Positron Annihilation Techniques", Trina C. Veals, Hampton University MS Thesis April (1993).

V. List of all participated Scientific Personnel
under
NASA Grant No. NAG1-1168
Period Oct 1, 1990 - Sept 30, 1996

Name	Title	Period
K. S. Han (Principal Investigator, Professor)		Oct 1, 1990 - present
Abe Eftekhari (Co-PI, Research Professor)		Oct 1, 1990 - Sept 30, 1995
T. Shin (Research Assistant, graduate)		June 1, 1991 - Aug 31, 1991
Trina Veals (Research Assistant, graduate)		Sept 1, 1991 - Aug 31, 1994
S.W. Lee (Research Assistant, graduate)		Oct 1, 1994 - Dec 31, 1995
Keisha N. Dumas-Hough (Research aide, undergraduate)		May 1, 1994 - May 31, 1995
Michael Lucas (Research aide, Undergraduate)		June 1, 1994 - May 31, 1995

VI. List of Appendix

1. "Free volume model for molecular weights of polymers", J. J. Singh and A. Eftekhari, Nuclear Instruments and Methods in Physics Research B63 477-483 (1992) .
2. "Free Volume Variation with Molecular Weight of Polymers" J. J . Singh, Abe Eftekhari, Jeffrey A Hinkley, Terry L. St. Clair, and Brian J. Jenson, NASA Tech. Memo. 4326 (Feb (1992)).
3. "Free Volume in Glassy Poly (arlene ether ketone)s", J. A. Hinkley, A. Eftekhari, R. A. Cook, B. J. Jenson and J. J. Singh, J. Poly. Sci-Poly. Vol. 30, pp. 1199-1198, 1992.
4. "Free Volume Characteristics of Epoxies ", Jag. J. Singh, Abe Eftekhari, William J. Schultz and Terry L. St. Clair, NASA Tech. Memo 4390. Sept (1992).
5. "Low Energy Positron Flux Generator for Microstructural Characterization of Thin Films", J.J.Singh, A. Eftekhari and T. L. St. Clair, Material Science Forum Vols. 105-110, pp 1985-1988 (1992).
6. "Microstructural Characterization of Thin Polymer Films by Positron Lifetime Spectroscopy", A. Eftekhari, A. K. St. Clair, D. M. Stoakley, Danny R. Sprinkly and J. J. Singh, ACS. Symposium Series 537, Ch38 536-545 (1994)
7. "Positron Lifetime Spectroscopy for Investigation of thin Polymer Coatings" Jag. J. Singh, Abe Eftekhari and Danny R. Sprinkle, NASA Tech, Memo 4421 Feb. (1993).



51-27

027722

076816

9f.

Appendix 2

"Free Volume Variation with Molecular Weight of Polymers" J. J. Singh, Abe Eftekhari, Jeffrey A Hinkley, Terry L. St. Clair, and Brian J. Jenson, NASA Tech. Memo. 4326 (Feb (1992).

NASA Technical Memorandum 4326

Free Volume Variation With Molecular Weight of Polymers

Jag J. Singh
Langley Research Center
Hampton, Virginia

Abe Eftekhari
Hampton University
Hampton, Virginia

Jeffrey A. Hinkley, Terry L. St. Clair,
and Brian J. Jensen
Langley Research Center
Hampton, Virginia

NASA

National Aeronautics and
Space Administration

Office of Management

Scientific and Technical
Information Program

1992

Abstract

Free volume measurements have been made in several molecular weight fractions of two different geometries of poly(arylene ether ketone)s. Free volumes were measured using positron lifetime spectroscopy. It has been observed that the free volume cell size V_f varies with the molecular weight M of the test samples according to an equation of the form $V_f = AM^B$, where A and B are constants. The molecular weights computed from the free volume cell sizes are in good agreement with the values measured by gel permeation chromatography.

Introduction

All polymers generally have regions of low atomic density (free volume cells) resulting from geometrical mismatch among neighboring molecular chains/segments. The sizes and concentrations of these free volume cells depend on the polymer molecular architecture and affect many physical properties of high polymers. For example, we have recently shown (ref. 1) that both the solubility coefficient as well as the diffusion coefficient for gaseous molecules are modified by the presence of free volume cells in the test polymers. As a result, the presence of free volume cells in the test polymers enhances the permeation of gases through them. Similarly, the free volume cells in polymeric materials affect their other thermodynamic properties. The free volume cell sizes change markedly at the phase transition temperatures of the test polymers. Thus, the large differences in thermal expansion coefficients observed above and below the glass transition temperatures arise from the large free volume expansion at the glass transition temperatures. The rapid decrease of free volume cell size with increase in pressure above the glass transition temperature also accounts for the observed trends in the compressibility of polymeric materials as a function of temperature. It is also noted that positron lifetime spectroscopy separates free volume compressibility from the compressibility of the excluded volume of the test polymers. Many conventional techniques can yield (ref. 2) only a total compressibility that includes both effects.

It thus appears that the free volume plays an important role in determining physical properties of the polymeric materials. In the case of linear polymers, a relationship between the free volume cell size and the molecular weight of the polymer can be developed. Let the molecular weight of the polymer be M . Then n moles of the polymer shall weigh $nM = M_1$ and

$$M_1 = \rho V \quad (1)$$

where ρ is the density of the polymer and V is the volume occupied by the polymer when it has zero free volume.

If the polymer has a free volume ΔV then the total volume occupied by the polymer is $V + \Delta V$. Then we have

$$M_1' = \rho V + \rho'(\Delta V) \quad (2)$$

where ρ' is the density of the medium occupying ΔV . Equation (2) can be rearranged as follows:

$$\begin{aligned} M_1' &= \rho V \left(1 + \frac{\rho' \Delta V}{\rho V} \right) \\ &= \rho V \left(1 + \alpha \frac{\Delta V}{V} \right) \end{aligned} \quad (3)$$

where $\alpha = \rho'/\rho = \text{Constant}$ for a polymer system. Rewriting equation (3), we have

$$\begin{aligned} M_1 + \Delta M_1 &= M_1 \left(1 + \alpha \frac{\Delta V}{V} \right) \\ \frac{\Delta M_1}{M_1} &= \alpha \frac{\Delta V}{V} \\ \frac{\Delta M}{M} &= \alpha \frac{\Delta V}{V} \end{aligned} \quad (4)$$

$$\frac{\Delta M}{M} = \alpha f \quad (5)$$

where $f = \text{Free volume fraction} = CI_3V_f$, C is the polymer structural constant, I_3 is the intensity of the third (longest) positron lifetime component, and V_f is the free volume cell size. Thus, equation (5) becomes

$$\begin{aligned} \frac{\Delta M}{M} &= (\alpha C)I_3V_f \\ &= (\beta I_3)V_f \end{aligned} \quad (6)$$

where $\beta = \alpha C$. Since I_3 and V_f are independent variables, equation (6) can be written as follows:

$$\psi_1(M) = D\psi_2(V_f) \quad (7)$$

where $D = \beta I_3$ is a constant related to electron density/momentum distribution and the architecture of the test polymer. It thus appears that the free volume cell size V_f is a function of M . The relationship between V_f and M can be expressed as follows:¹

$$V_f = AM^B \quad (8)$$

¹ Preliminary results based on this formalism have been reported previously. (See ref. 3.)

where A and B are constants for the test polymer and are expected to be independent of its degree of polymerization. However, they depend on the temperature and pressure of the sample environment.

Equation (8) is quite similar in form to the Mark-Houwink equation relating the intrinsic viscosity $[\eta]$ and the molecular weight M of the polymer in solution (ref. 4). It can be extended to cross-linked polymers if M represents the weight of the polymer sample between two adjacent cross links. The purpose of this study is to make a systematic investigation of V_f versus M in selected linear polymers. Poly(arylene ether ketone)s (PAEK) of variable molecular weights were selected as the test polymers. The free volume V_f values were measured using positron lifetime spectroscopy (PLS). All measurements were made at room temperature and atmospheric pressure.

Experimental Procedure

Sample Preparation

The structures of poly(arylene ether ketone)s chosen for study are shown in figure 1. It was anticipated that the different geometries of the two repeat units might lead to different packing behaviors and hence different free volumes. Details of their syntheses and fractionation have been reported earlier (ref. 5). Several molecular weight fractions were studied in an effort to discern possible effects of chain ends. Molecular weights of the various fractions differed by over a factor of 4, although, as nearly as could be determined, the specific volumes of both polymers were practically independent of molecular weights in this range (table I).

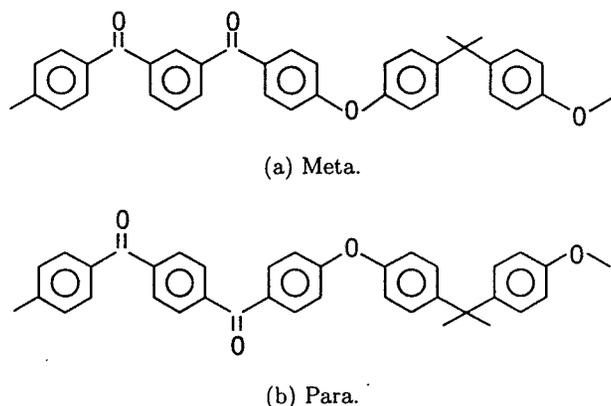


Figure 1. Structure of meta- and para-poly(arylene ether ketone)s.

Thin ($30\ \mu\text{m}$) films for the positron lifetime studies were prepared by casting them on glass plates

from *m*-cresol solution. These films were air dried for 2 days in a low-humidity enclosure, then gradually heated in an air-circulating oven to 250°C , which is well above the polymer glass transition temperature T_g . Finally, they were cooled rapidly to room temperature by removing the plates from the oven and placing them on a cool surface. Wide angle X-ray scattering showed the films to be free of detectable crystallinity.

Positron Lifetime Measurements

Positron lifetime measurements were made using a standard fast-fast coincidence timing technique. The coincidence system time resolution was of the order of 225 psec. All measurements were made at room temperature and atmospheric pressure. Typical spectrum accumulation time was ≈ 6 hr with a $50\ \mu\text{C}$ Na^{22} positron source. This accumulation time provided excellent counting statistics—namely 10^6 counts in the peak channel. Figure 2 shows a typical lifetime spectrum in para-PAEK films. Figure 3 shows a typical spectrum in meta-PAEK films. Lifetime spectra were analyzed using PAPLS (ref. 6) and POSITRONFIT EXTENDED (ref. 7) computer programs. In all cases, three-component analyses gave the best fits to the experimental spectra.

Experimental Results

Results in PAEK Films

The positron lifetime results in para-PAEK films are summarized in table II; τ_1 , I_1 and τ_2 , I_2 refer to the lifetime and intensity of the first and second components, respectively. The longest component lifetime (τ_3) results from orthopositronium annihilation. The lifetime (τ_3) and its intensity (I_3) are related to the free volume cell size V_f as follows (ref. 8):

$$\frac{1}{2\tau_3} = \left(1 - \frac{R}{R_o} + \frac{1}{2\pi} \sin \frac{2\pi R}{R_o} \right) \quad (9)$$

where

- τ_3 longest component lifetime, nsec
- R free volume cell radius, nm
- $R_o = (R + \Delta R)$, nm

(The best fitted value of ΔR for all known data has been reported to be 0.1659 nm. See ref. 8.)

The free cell volume V_f is given by $\frac{4}{3}\pi R^3$. The V_f values for various para-PAEK samples are summarized in table III. The positron lifetime results in meta-PAEK films are summarized in table IV. The corresponding V_f values are summarized in table V.

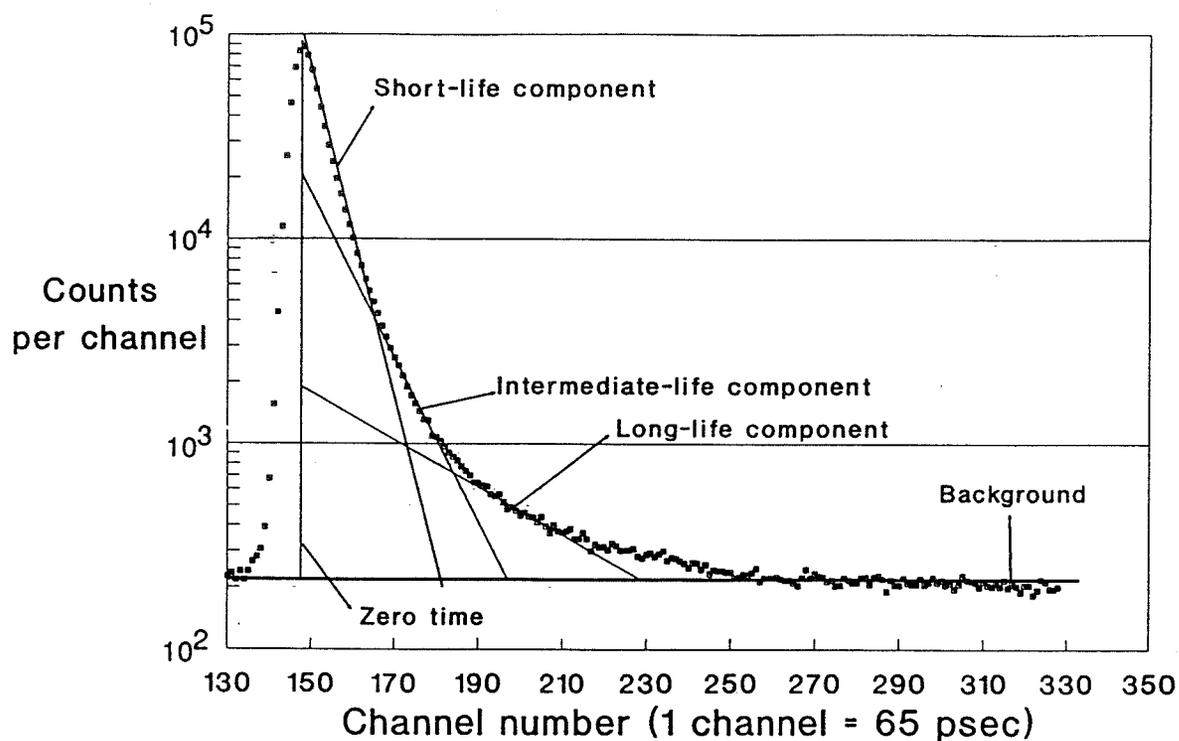


Figure 2. Typical lifetime spectrum in para-PAEK films.

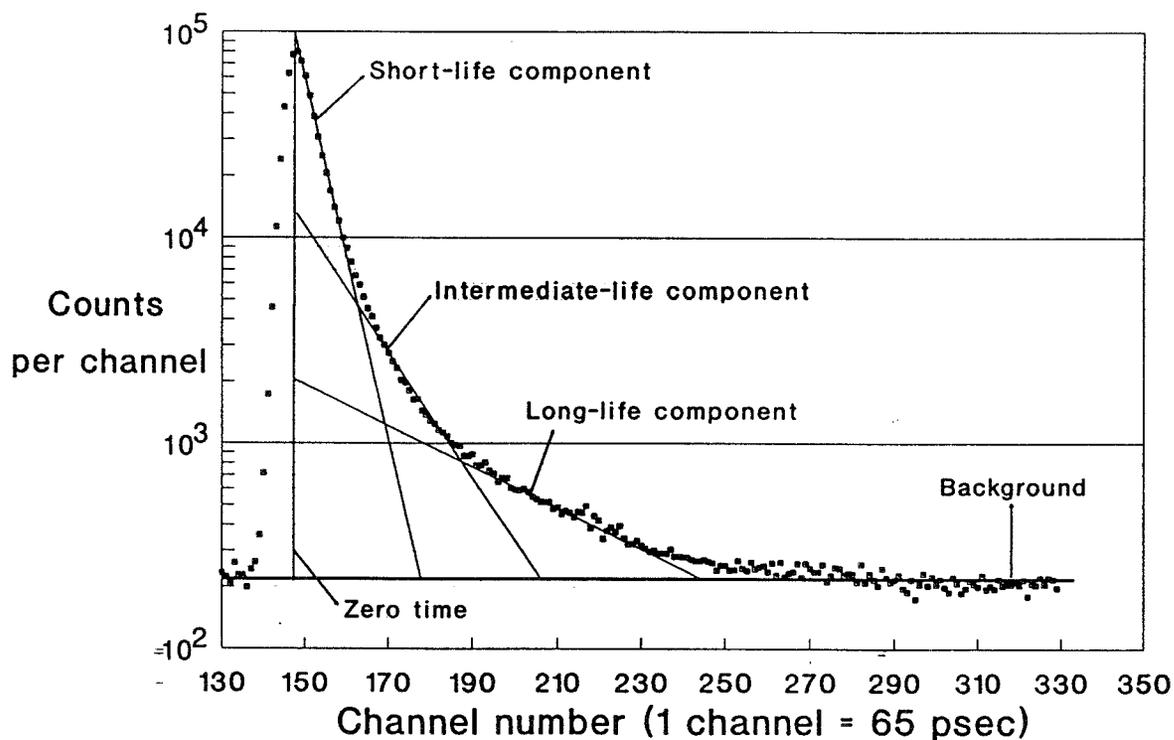


Figure 3. Typical lifetime spectrum in meta-PAEK films.

In addition to the values of V_f , measured values of saturation moisture content v/o in the test films have also been included in tables III and V.

The free volume fraction f in the test films can be calculated as follows:

$$f = CI_3V_{f3} \quad (10)$$

where V_{f3} is the free volume cell size associated with the third lifetime component.

If one assumes that water enters the test films physically, the values of C can be easily calculated by equating f with the corresponding saturation moisture content v/o . This, however, may not always be the case. In some cases, the presence of hydrophobic atoms in the polymer chains may inhibit water entry in the free volume cells, as reported by Singh et al. in a recent study of contact lens polymers (ref. 1). In others, water may enter the polymer system chemically as well as physically, thus making the saturation moisture content v/o exceed the free volume fraction (ref. 9). A small concentration of microdefects above the size of the PLS limit ($R \geq 5 \text{ \AA}$) can also cause v/o to exceed f . Nevertheless, v/o should often provide a good first-order approximation for f .

Calculation of the Molecular Weights

In order to obtain the values of A and B in equation (8), experimental values of the molecular weights (M_n) of the test films were determined using the gel permeation chromatography/low angle laser light scattering (GPC/LALLS) technique (ref. 5). There were five para-PAEK samples and three meta-PAEK samples of different molecular weights. We used experimental molecular weights of three para-PAEK samples to determine the constants A and B by least-squares method. These constants were then used to predict the molecular weights of the remaining two samples. Similarly, two experimental molecular weights of the meta-PAEK samples were used to determine the structural constant A . The constant B is expected to remain unchanged.² The meta A and B combination of constants was then used to predict the molecular weight of the third meta sample. Comparisons between the experimental and calculated M_n values for the two systems are summarized in tables III and V, respectively. It is apparent that the agreement is quite good for both polymer systems. This indicates that equation (8) represents

² By considering all five para-PAEK and all three meta-PAEK samples, it has been determined that the constant B is the same for all PAEK samples, as expected from the theoretical arguments presented earlier

the correct form of relationship between V_f and M . The results are illustrated in figure 4.

Equation (8) should be applicable for the entire range of orthopositronium lifetimes observed in linear polymers—namely, 0.7–3.5 nsec. These lifetimes correspond to molecular weights ranging from 4000 to 200 000 g/mole.

Discussion

From the data presented above, it appears that V_f values track the M_n values of the test polymers quite well. As expected, a unique set of A and B values predict the test polymer M_n values as long as their molecular structure remains unchanged. A change in structure as we go from para-PAEK to meta-PAEK necessitates a different set of constants. A notable feature is the fact that V_f values are much larger in the meta geometry than the para geometry. However, this is consistent with the different packing behavior of the two geometries.

It has been reported (ref. 10) that as the molecular weights of most linear polymers decrease, their free volumes increase. The free volume fraction is given by CI_3V_f , as indicated in equation (10). It would thus appear that I_3V_f would decrease with increasing molecular weight of the test samples. This, however, is not the case in the samples investigated. Similarly, the trend in the change in the specific volume ($1/\rho$) with the molecular weight is also contrary to the reported behavior (ref. 10). Thus, both the I_3V_f and $1/\rho$ values exhibit trends with increasing molecular weights that are contrary to the reported behavior in most linear polymers. The glass transition temperatures T_g , on the other hand, increase with increasing molecular weights in agreement with the reported trends (ref. 10). These results are quite intriguing, though not inconsistent with the morphologies of the test polymers.

A further corroboration of the validity of the Free Volume Model was obtained by comparing the Mark-Houwink (M-H) (ref. 3) and Free Volume Model constants. The results are summarized in table VI. Clearly, the M-H and Free Volume Model exponential constants exhibit similar behavior when the repeat unit geometries change.

Concluding Remarks

It has been demonstrated that positron lifetime spectroscopy (PLS) may provide a reasonably accurate technique for measuring molecular weights of polymeric materials. However, the number of test samples in the present study was rather limited. The proposed model will have to be tested on a larger

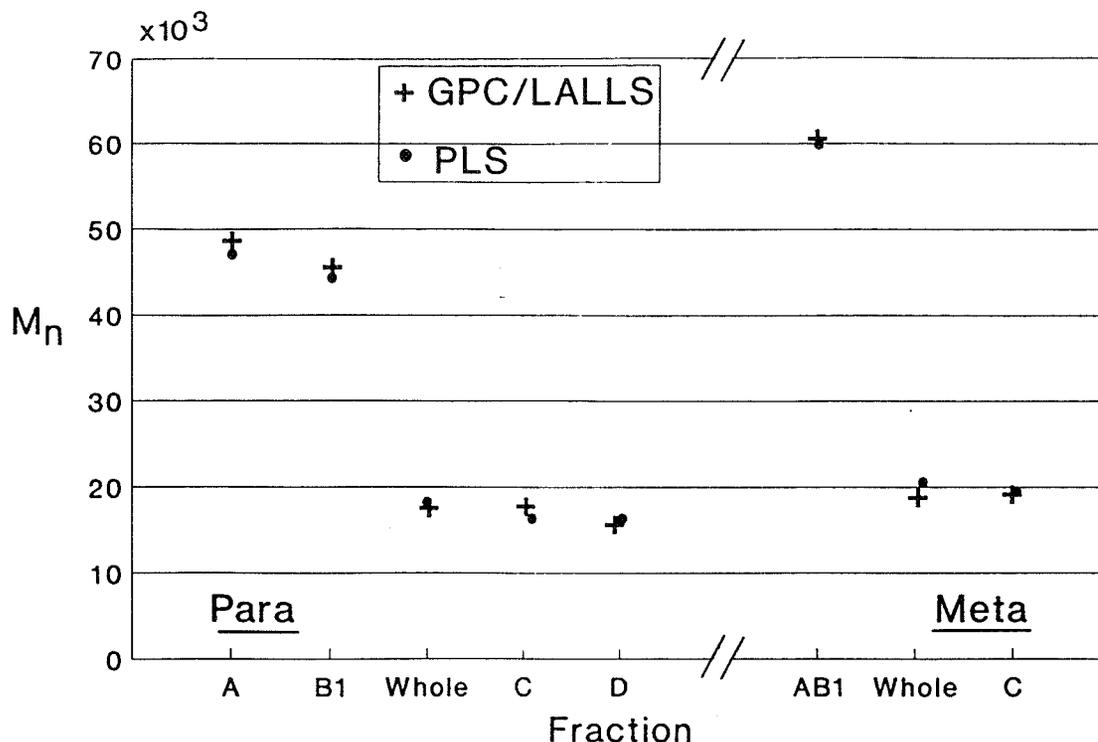


Figure 4. Comparison between molecular weights determined by GPC/LALLS and PLS methods.

number of a variety of samples before it becomes accepted. The proposed technique relates the free volume cell size V_f with the sample molecular weight M in a manner remarkably similar to that obtained by Mark-Houwink (M-H) relating the inherent viscosity $[\eta]$ and the molecular weight of the polymer solution. However, the M-H procedure requires the sample to be in liquid form. The PLS technique has been verified for two geometries of the poly(arylene ether ketone)s, where it not only predicts, with reasonable accuracy, the higher V_f values (i.e., looser packing) for the meta geometry, but also verifies anticipated structural change.

NASA Langley Research Center
Hampton, VA 23665-5225
December 20, 1991

References

1. Singh, Jag J.; Eftekhari, Abe; Upchurch, Billy T.; and Burns, Karen S.: Free Volume in Contact Lens Polymers. *Third International Workshop on Positron and Positronium Chemistry*, Y. C. Jean, ed., World Scientific Publ. Co., Inc., 1990, pp. 54-61.
2. Jean, Y. C.: Free-Volume Hole Properties of Polymers Probed by Positron Annihilation Spectroscopy. *Third International Workshop on Positron and Positronium Chemistry*, Y. C. Jean, ed., World Scientific Publ. Co., Inc., 1990, pp. 1-29.
3. Singh, Jag J.; Eftekhari, Abe; and St. Clair, Terry L.: *A Study of Physical Properties of ODPa-p-PDA Polyimide Films*. NASA TM-102625, 1990.
4. Seymour, Raymond B.; and Carraher, Charles E., Jr.: *Structure-Property Relationships in Polymers*. Plenum Press, c.1984.
5. Hinkley, J. A.; Crook, R. A.; and Davis, J. R. J.: Chain Dimensions and Rheology of Poly(arylene ethers). *High Perform. Polymers*, vol. 1, no. 1, 1989, pp. 61-71.
6. Singh, Jag J.; Mall, Gerald H.; and Sprinkle, Danny R.: *Analysis of Positron Lifetime Spectra in Polymers*. NASA TP-2853, 1988.
7. Kirkegaard, P.: Positronfit Extended: A New Version of a Program for Analysing Positron Lifetime Spectra. *Comput. Phys. Commun.*, vol. 7, no. 7, July 1974, pp. 401-409.
8. Nakanishi, H.; Wang, S. J.; and Jean, Y. C.: Microscopic Surface Tension Studied by Positron Annihilation. *International Symposium on Positron Annihilation Studies of Fluids*, Suresh C. Sharma, ed., World Scientific Publ. Co., Inc., 1988, pp. 292-298.
9. Singh, Jag J.; St. Clair, Terry L.; Holt, William H.; and Mock, Willis, Jr.: Moisture Dependence of Positron Annihilation Spectra in Nylon-6. *Nucl. Instrum. & Methods Phys. Res.*, vol. 221, no. 2, Apr. 1, 1984, pp. 427-432.
10. Liu, Xijun; Chen, Donglin; He, Zhiduan; Zhang, Hao; and Hu, Huizhen: Molecular Weight Dependence of Glass Transition of Cyclic Polystyrene. *Polymer Commun.*, vol. 32, no. 4, 1991, pp. 123-125.

Table I. Characteristics of Polymer Fractions (ref. 5)

Sample	* M_n	† M_n	M_w	ρ , g/cm ³	η_{inh} , dl/g	T_g , °C
Para						
Whole polymer		19.0×10^3	26.0×10^3	1.2058	0.50	
Fraction A	29.6×10^3	47.0	51.0	1.2060	.78	165
Fraction B1	28.4	44.5	45.9	1.2041	.70	163
Fraction C	15.4	17.6	18.3	1.2052	.37	159
Fraction D	17.8	16.3	16.9	1.2061	.38	160
Meta						
Whole polymer		20.8×10^3	26.6×10^3	1.2072	0.39	148
Fraction AB1	47.3×10^3	60.8	66.0	1.2077	.65	153
Fraction C	20.3	19.8	21.0	1.2074	.35	148

*End group analysis.

†Gel permeation chromatography/low angle laser light scattering technique. These values have an error of ± 10 percent.

Table II. Positron Lifetime Parameters in Para-Poly(Arylene Ether Ketone) Films

Geometry	τ_1 , psec	I_1 , %	τ_2 , psec	I_2 , %	τ_3 , psec	I_3 , %
Whole polymer	187 ± 12	37 ± 3	409 ± 16	59 ± 3	905 ± 60	4 ± 1
Fraction A	171 ± 09	44 ± 3	407 ± 16	53 ± 2	1069 ± 70	3 ± 1
Fraction B1	139 ± 16	35 ± 4	371 ± 24	60 ± 2	1037 ± 70	6 ± 1
Fraction C	196 ± 08	41 ± 2	416 ± 20	56 ± 3	869 ± 75	3 ± 1
Fraction D	165 ± 17	33 ± 5	390 ± 24	63 ± 3	850 ± 65	4 ± 1

Table III. Summary of V_f Values in Para-Poly(Arylene Ether Ketone) Films

Sample	* M_n	$V_f, \text{\AA}^3$	** M_n
†Whole polymer	19.0×10^3	13.7 ± 0.6	$(21.3 \pm 1.5) \times 10^3$
†Fraction A	47.0	23.2 ± 0.7	51.3 ± 2.4
†Fraction B1	44.5	21.3 ± 0.6	43.2 ± 1.9
†Fraction C	17.6	12.1 ± 0.8	17.5 ± 1.9
†Fraction D	16.3	11.2 ± 0.9	15.5 ± 2.0

* M_n values were determined by gel permeation chromatography/low angle laser light scattering technique. All values have an error of ± 10 percent.

** M_n values are calculated by using the equation $V_f = AM_n^B$, where $A = 2.70 \times 10^{-2}$ and $B = 0.625$.

†These three samples were used to calculate the constants A and B .

†The molecular weights of these samples were calculated using the values of A and B computed above.

Table IV. Positron Lifetime Parameters in Meta-Poly(Arylene Ether Ketone) Films

Geometry	τ_1 , psec	I_1 , %	τ_2 , psec	I_2 , %	τ_3 , psec	I_3 , %
Whole polymer	183 \pm 4	51 \pm 2	442 \pm 8	43 \pm 1	1698 \pm 40	6 \pm 1
Fraction AB1	211 \pm 3	59 \pm 1	516 \pm 23	36 \pm 1	2273 \pm 77	5 \pm 1
Fraction C	181 \pm 7	46 \pm 3	433 \pm 12	47 \pm 2	1651 \pm 52	7 \pm 1

Table V. Summary of V_f Values in Meta-Poly(Arylene Ether Ketone) Films

Sample	* M_n	V_f , \AA^3	** M_n
‡Whole polymer	20.8 $\times 10^3$	70.8 \pm 0.4	(22.8 \pm 0.2) $\times 10^3$
†Fraction AB1	60.8	130.2 \pm 0.4	60.3 \pm 0.3
†Fraction C	19.8	66.2 \pm 0.6	20.4 \pm 0.3

* M_n values were determined by gel permeation chromatography/low angle laser light scattering technique. All values have an error of ± 10 percent.

** M_n values are calculated by using the equation $V_f = AM_n^B$, where $A = 1.340 \times 10^{-1}$ and $B = 0.625$.

†These two samples were used to calculate the constant A .

‡The molecular weight of this sample was calculated using the value of A computed above.

Table VI. Summary of Mark-Houwink and Free-Volume Equation Constants

$$\left[\begin{array}{l} \text{Mark-Houwink Equation: } [\eta] = KM^a \\ \text{Free Volume Model: } V_f = AM^B \end{array} \right]$$

Sample	Mark-Houwink equation		Free-volume model	
	K	a	A	B
Para-PAEK	1.20 $\times 10^{-3}$	0.60	2.70 $\times 10^{-2}$	0.625
Meta-PAEK	9.00 $\times 10^{-4}$	0.60	1.34 $\times 10^{-1}$	0.625

52-27 NDB

027723

076824

5P.

Appendix 3

"Free Volume in Glassy Poly (arylene ether ketone)s", J. A. Hinkley, A. Eftekhari, R. A. Cook, B. J. Jenson and J. J. Singh, J. Poly. Sci-Poly. Vol.30, pp. 1199-1198, 1992.

Free Volume in Glassy Poly(arylene Ether Ketone)s

J. A. HINKLEY,¹ A. EFTEKHARI,² R. A. CROOK,³ B. J. JENSEN,¹ and J. J. SINGH¹

¹NASA Langley Research Center, Hampton, Virginia 23665-5225; ²Hampton University, Hampton, Virginia 23666; ³Texas A&M University, College Station, Texas 77843

SYNOPSIS

Amorphous polyarylene ether ketones were examined in the glassy state by positron annihilation lifetime spectroscopy (PALS) and in the melt by standard rheological techniques. Specimens were well-characterized fractions of two isomeric structures. PALS clearly shows that the polymer with meta linkages in its backbone contains larger voids (> 0.25 nm radius). Thus despite their similar bulk densities, the two materials must pack very differently on a local scale. On the other hand, the free volumes inferred from the WLF treatment of melt viscosity data are practically identical in both materials ca. 4% at T_g . The comparison between techniques sheds some light on the distribution of free volume.

© 1992 John Wiley & Sons, Inc.

Keywords: free volume in glassy poly(arylene ether ketone)s • glassy polymers, free volume in • poly(arylene ether ketone)s, free volume in

INTRODUCTION

The free volume concept has great intuitive appeal, and arises quite naturally in light of the discontinuity in expansion coefficient that occurs at T_g . It provides qualitative explanations for the dependence of T_g on molecular weight, diluent and pressure, and the dependence of viscoelastic relaxation times on temperature, pressure,¹ static tensile strain,² and antiplasticization.³ It also is invoked in treatments of densification and embrittlement (physical aging).⁴ Despite this utility, the free volume per gram, v_f , remains poorly defined operationally. Different theories derive widely differing values. Furthermore, some phenomena clearly require more than a single volume parameter for their explanation.⁵

Positron annihilation lifetime spectroscopy (PALS) was employed to probe the effects of detailed chain architecture on free volume. The results are compared with parameters derived from a standard treatment of viscoelasticity.

MATERIALS

The polyarylene ether ketones chosen for study are shown in Figure 1. It was anticipated that the dif-

ferent geometries of the two repeat units might lead to different packing behavior and hence different free volumes. Details of their synthesis and fractionation have been reported earlier.⁶ Several molecular weight fractions were studied in an effort to discern possible effects of chain ends. Molecular weights of the various fractions differed by more than a factor of 5.

EXPERIMENTAL

Characterization data for the various polymer fractions are given in Table I. Number-average molecular weights were determined by gel permeation chromatography (GPC) light scattering; densities were measured at 25°C using a flotation technique in aqueous $ZnCl_2$.

Dynamic mechanical data were obtained on compression-molded discs using a Rheometrics System IV rheometer in oscillatory parallel-plate mode. Strain sweeps verified that data were obtained in the linear range. Time-temperature shift factors were obtained by horizontally shifting data from different temperatures on a log-log plot until they could be superposed. Within the range $T_g < T < T_g + 90^\circ C$ the shift factors a_T fit the WLF equation.¹

$$\log a_T = -c_1^0(T - T_0)/(c_2^0 + T - T_0) \quad (1)$$

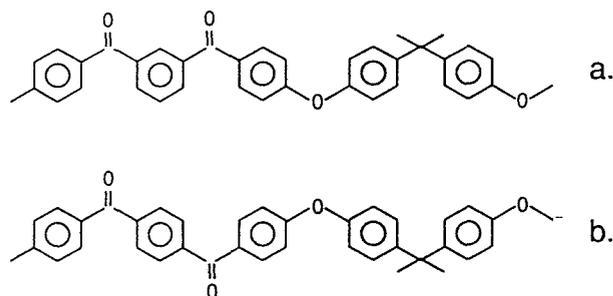


Figure 1. Chemical structures of polymers studied. (a) meta polymer, (b) para polymer.

In this equation, T_0 is an arbitrary reference temperature within the measurement range and c_1^0 and c_2^0 are constants at that temperature, derived from a linear least-squares fit to a plot of $(T - T_0)/\log a_T$ versus $T > T_0$.

Thin (30 μm) polymer films for positron annihilation studies were prepared by casting on glass plates from *m*-cresol solution. The films were air-dried for 2 days in a low-humidity enclosure, then gradually heated in an air-circulating oven to above T_g . After a brief exposure at 250°C to remove any solvent residue, they were cooled rapidly to room temperature by removing the plates from the oven and placing them on a cool surface. Wide-angle x-ray scattering showed the films to be free of detectable crystallinity. Glass transition temperatures were determined by differential scanning calorimetry (DSC) at a heating rate of 20°C/min.

Positron lifetimes in single films were measured at room temperature using a recently developed slow-positron flux generator⁷ and standard fast-fast

Table I. Polyarylene Ether Ketone Fractions

	$M_n \times 10^{-3}$	Film density (g/cm ³)
<i>meta</i>		
Fraction AB1	60	1.207 ₇
Fraction C	20	1.207 ₄
Fraction D	13	1.208 ₅
Fraction F	8	—
Whole polymer	21	1.206 ₂
<i>para</i>		
Fraction A	47	1.206 ₀
Fraction B1	44	1.204 ₁
Fraction C	16	1.205 ₂
Fraction D	16	1.206 ₁
Fraction F	9	—
Whole polymer	19	1.205 ₈

coincidence timing technique. Lifetime spectra were analyzed using PAPLS⁸ and POSFIT EXTENDED⁹ computer programs. After correction for the instrument response, the total intensity I was found to fit an expression of the form

$$I = B + \sum_{j=1}^n I_j e^{-t/\tau_j}$$

with $n = 3$. The first two exponentials had lifetimes of approximately 180 and 400 ps, respectively; the third, much longer, component τ_3 was assigned to annihilation of *ortho*-positronium residing in free volume cells in the test film. The size of these cells can be estimated using the equation of Nakanishi et al.¹⁰

RESULTS AND DISCUSSION

A typical set of rheological master curves is shown in Figure 2; the corresponding shift factors and the WLF fit to them are given in Figure 3. According to an interpretation derived from the Doolittle equation for liquid viscosity,¹ the constants in the WLF equation are given as

$$c_1^0 = B/2.303 f_0$$

$$c_2^0 = f_0/\alpha_f$$

Therefore, if a value is assumed for B , then f_0 , the fractional free volume at the reference temperature and α_f , the expansion coefficient of the free volume may be obtained from these equations. Although other choices are possible,¹¹ we follow the usual rather arbitrary practice of setting $B = 1$. Reference

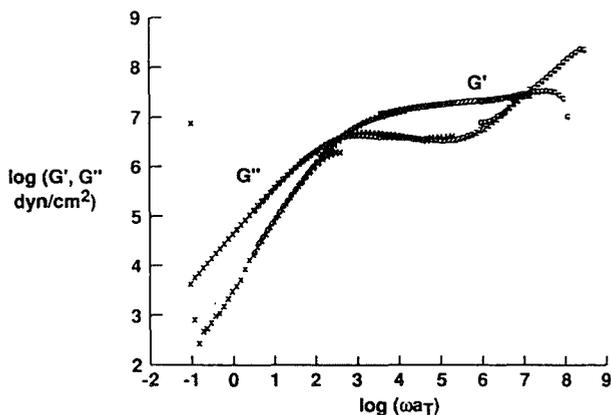


Figure 2. Master curves for para fraction B1 at reference temperature of 210°C.

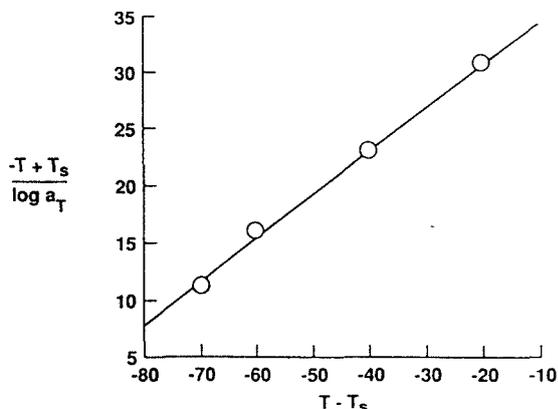


Figure 3. Shift factors derived from the data in Figure 2. Least-squares fit gives WLF constants according to eq. (1).

temperatures may be adjusted from T_0 to T_g using the relationships

$$c_1^g = c_1^0 c_2^0 (c_2^0 + T_g - T_0)$$

$$c_2^g = c_2^0 + T_g - T_0 \quad (2)$$

The resulting values of the free-volume parameters are collected in Table II.

The fractional free volume at T_g , designated f_g , is seen to be somewhat larger for our materials than the figure (0.025) obtained using the "universal" values of the WLF constants. That figure is quoted as characteristic of the majority of vinyl and diene polymers;¹ one could argue that the bulkiness of our polymer may account for the slightly larger f_g . The thermal expansion coefficients α_f inferred from eq. (2) also are larger than those of most vinyl polymers; however this probably is not too surprising either, given the higher T_g s of our materials. Neither f_g nor α_f shows a clear trend with regard to molecular weight.

Of great interest is the fact that the average free volumes, f_g , calculated for meta and para polymers are the same, within the experimental scatter. On the basis of these results, then, one cannot attribute the lower viscosity⁶ of the meta polymer to a difference in packing between the two polymers. In fact, the present results might support the notion that T_g is an iso-free volume state.

Before proceeding to a discussion of the room temperature positron lifetimes, we note that within the framework of the WLF interpretation, the relative values in Table II should also characterize the glassy state, even well below T_g . This is because the choice $B = 1$ implies that the change in expansion coefficient at T_g is due entirely to expansion of free volume. In other words, the free volume is approximately constant below T_g .

The key results of the positron experiments are assembled in Table III. We note first of all that for both polymers, τ_3 seems to increase with molecular weight. Although the reason for this is not clear, a similar trend has been found in this laboratory for other glassy polymers.¹²

Comparing the results from the two isomeric structures, we observe that at equivalent molecular weights, τ_3 is approximately twice as large in the meta polymer as in the para analog. This translates to an effective hole radius about 1.7 times as large. Since the volume associated with an individual free volume "cell" is $v_p = (4/3)\pi R^3$, the quantity $v_p I_1$ given in the last column of Table III should be proportional to the total free volume. Unfortunately, the proportionality constant is unknown, and it may well be different for different polymers. Nevertheless, it appears that the total void volume as well as the average void size probed by the positronium may be considerably larger in the meta polymer. One might have anticipated that the meta structure

Table II. WLF Parameters with T_g as Reference Temperature

Fraction	T_g	c_1^g	c_2^g	$f_g \times 10^2$	$\alpha_f \times 10^4$
Meta-AB1	153	10.81	21.67	4.02	18.5
C	148	11.07	42.25	3.92	9.3
D	146	10.11	23.36	4.29	18.4
F	138	11.18	34.74	3.88	11.2
				$4.03 \pm .18$	14.4 ± 4.8
Para-A	165	10.28	25.67	4.22	16.5
B1	163	11.26	21.40	3.86	18.0
D	160	10.10	25.74	4.30	16.7
F	151	10.13	36.99	4.29	11.6
				$4.18 \pm .20$	15.7 ± 2.8

Table III. Summary of *o*-Positronium Pick-off Results

	τ_3 (ps)	I_3 (%)	R (nm)	v_p (nm ³)	$v_p I_3 \times 10^3$
<i>meta</i>					
Fraction AB1	2273 ± 77	5 ± 1	.309	.123	6.2
Fraction C	1651 ± 52	7 ± 1	.251	.066	4.6
Whole polymer	1698 ± 40	6 ± 1	.256	.070	4.2
<i>para</i>					
Fraction A	1069 ± 70	3 ± 1	.177	.023	0.7
Fraction B1	1037 ± 70	6 ± 1	.172	.021	1.3
Fraction C	869 ± 75	3 ± 1	.142	.012	0.4
Fraction D	850 ± 65	4 ± 1	.139	.011	0.4
Whole polymer	905 ± 60	4 ± 1	.150	.014	0.6

would be harder to pack because of its irregularity, but the magnitude of the difference is quite striking. The inescapable conclusion is that on a scale of a few Angstroms, the local structure of the glass is directly influenced by the chain architecture.

This localized effect may be reconciled with the rheological results by comparing the measured hole sizes v_p with characteristic molecular dimensions. In a polymer melt, rearrangement of a chain contour occurs by the motion of a segment consisting of several rotatable bonds. In our resins, such a segment would correspond in size to several benzene rings. The average size of the holes sampled by the positron experiment, on the other hand, is smaller than the 0.08 nm³ van der Waals volume of benzene.¹³ It is clear therefore that most of the holes sampled by PALS are not accessible for main-chain motion.

CONCLUSION

It is easy to show^{14,15} that the empty or unoccupied volume in polymer glasses amounts to about 30% of the total volume, almost without regard to differences in the chemical structures of the chains. A knowledge of how this volume is distributed is important to the understanding of mechanical and transport properties. The present results indicate that local packing, on the scale of 0.1–0.3 nm, is quite sensitive to the regularity of the chain backbone in aromatic polymers. Although these local fluctuations are relatively unimportant to large-scale motions at T_g , they would probably affect other properties, such as permeation by small molecules.

Thanks are due to Carol Gautreaux for the wide-angle x-ray scans.

REFERENCES AND NOTES

1. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York, 1980, Chap. 11.
2. For example, S. Matsuoka, C. J. Aloisio, and H. E. Bair, *J. Appl. Phys.*, **44**, 4265 (1973).
3. For example, J. S. Vrentas, J. L. Duda, and H-C. Ling, *Macromolecules*, **21**, 1470 (1988).
4. J. J. Curro and R. J. Roe, *Polymer*, **25**, 1424 (1984).
5. R. E. Robertson, R. Simha, and J. G. Curro, *Macromolecules*, **17**, 911 (1984).
6. J. A. Hinkley, R. A. Crook, and J. R. J. Davis, *High Perform. Polym.*, **1**, 61 (1989).
7. J. J. Singh, A. Eftekhari, and T. L. St. Clair, *Nucl. Instrum. Meth. Phys. Res.*, **B53**, 342 (1991).
8. J. J. Singh, G. H. Mall, and D. R. Sprinkle, "Analysis of Positron Lifetime Spectra in Polymers," NASA Technical Paper 2853, 1988.
9. P. Kirkegaard, *Comput. Phys. Commun.*, **7**(7), 401 (1974).
10. H. Nakanishi, S. J. Wang, and Y. C. Jean, in *Positron Annihilation in Fluids*, S. C. Sharma (ed.), World Scientific, Singapore, 1988, p. 292; also H. Nakanishi, Y. C. Jean, E. G. Smith, and T. C. Sandreczki, *J. Polym. Sci. (Phys)*, **27**, 1419 (1989).
11. G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5**, 261 (1967).
12. J. J. Singh, A. Eftekhari, and T. L. St. Clair, "A Study of Physical Properties of ODPa-p-PDA Polyimide Films," NASA Technical Memorandum No. 102625, March 1990.
13. A. Bondi, *J. Chem. Phys.*, **58**, 929 (1954).
14. R. N. Haward, in *The Physics of Glassy Polymers*, R. N. Haward (ed.), Wiley, New York, 1973, Chap. 1.
15. A. Bondi, *J. Polym. Sci.*, **A2**, 3159 (1964).

Received July 6, 1991

Accepted December 21, 1991

53-27

027724

01260

276827

14p.

Appendix 6

"Microstructural Characterization of Thin Polymer Films by Positron Lifetime Spectroscopy", A. Eftekhari, A. K. St. Clair, D. M. Stoakley, Danny R. Sprinkly and J. J. Singh, ACS. Symposium Series 537, Ch38 536-545 (1994)

ACS SYMPOSIUM SERIES **537**

Polymers for Microelectronics

Resists and Dielectrics

Larry F. Thompson, EDITOR
AT&T Bell Laboratories

C. Grant Willson, EDITOR
The University of Texas at Austin

Seiichi Tagawa, EDITOR
Osaka University

Developed from a symposium sponsored
by the Division of Polymeric Materials:
Science and Engineering, Inc., of the American Chemical Society
and the Society of Polymer Science, Japan,
at the 203rd National Meeting
of the American Chemical Society,
San Francisco, California,
April 5–10, 1992



American Chemical Society, Washington, DC 1994

Chapter 38

Microstructural Characterization of Thin Polyimide Films by Positron Lifetime Spectroscopy

A. Eftekhari¹, A. K. St. Clair², D. M. Stoakley², Danny R. Sprinkle², and J. J. Singh²

¹Department of Physics, Hampton University, Hampton, VA 23668

²National Aeronautics and Space Administration, Langley Research Center, M/S 235, Hampton, VA 23665-5225

Positron lifetimes have been measured in a series of thin aromatic polyimide films. No evidence of positronium formation was observed in any of the films investigated. All test films exhibited only two positron lifetime components, the longer component corresponding to the positrons annihilating at shallow traps. Based on these trapped positron lifetimes, free volume fractions have been calculated for all the films tested. A free volume model has been developed to calculate the dielectric constants of thin polyimide films. The experimental and the calculated values for the dielectric constants of the films tested are in reasonably good agreement. It has been further noted that the presence of bulky CF₃ groups and meta linkages in the polyimide structure results in higher free volume fraction and, consequently, lower dielectric constant values for the films studied.

Polyimides are an important class of polymers for high temperature aerospace applications. Thin polyimide films are ideal candidates for protective coatings on antenna reflectors and other electronic applications. Their properties, both physical and electrical, are expected to be strongly influenced by their morphology. We have developed a novel technique for monitoring microstructural characteristics of thin polymer films. It is based on the sensitivity of the positron lifetimes to the molecular architecture of the polymers. Specifically, positron lifetimes can be used to calculate free volume hole radii and free volume fractions in the test polymers. A free volume model has been developed to calculate dielectric constants of thin polyimide films. It has been tested on a series of special purpose polyimide films developed for aerospace communication networks. The results are described in the following sections.

EXPERIMENTAL TECHNIQUES

Materials

The aromatic polyimide films (1-3) used in this study are listed in Table I. The dianhydride monomers 2,2-bis(3,4-dicarboxy-phenyl)hexafluoropropanedian-

Table I. Physical and Electrical Properties of the Test Films

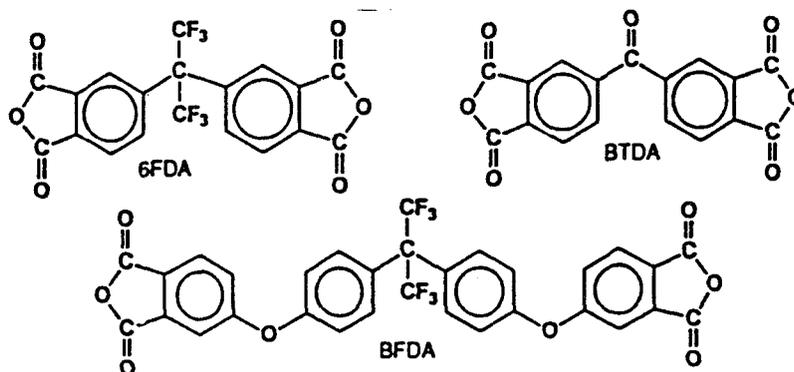
Sample	Density (gms/cc)	Sat. Moist Content, volume % (V/O) ^(*)	Dielectric Constant ϵ (at 10 GHz)
Kapton (Reference)	1.431	2.02	3.20 + 0.03
BFDA + ODA	1.384	0.74	2.63 ± 0.03
BFDA + 4-BDAF	1.400	1.38	2.44 ± 0.03
6FDA + DDSO ₂	1.486	0.74	2.86 ± 0.03
BFDA + DABTF	1.440	0.49	2.55 ± 0.03
6FDA + APB	1.434	0.53	2.71 ± 0.03
BTDA + ODA	1.380	1.21	3.15 ± 0.03

$$\begin{aligned}
 (*) \text{Saturation Moisture Volume Percent} &= V/O \\
 &= 100 \left(\frac{\text{Saturation Moisture Fraction by Volume}}{100} \right) \\
 &= \frac{100 \rho(W/O)}{100 + \rho(W/O)} \\
 &\text{where } W/O = \text{Saturation Moisture Weight Percent}
 \end{aligned}$$

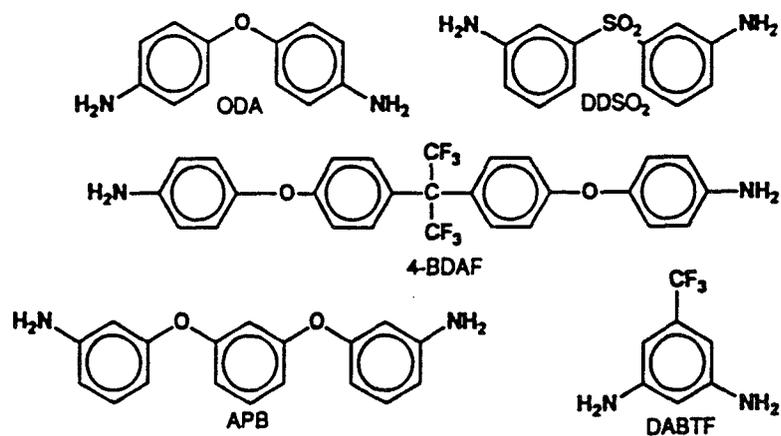
hydride (6FDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) were also obtained from commercial sources. The diamine monomers 4,4'-oxydianiline (ODA), 3,3'-diaminodiphenylsulfone (DDSO₂) and 1,3-bis(aminophenoxy)benzene (APB) were also obtained commercially. The bis[4-(3,4-dicarboxy-phenoxy) phenyl] hexafluoropropane dianhydride (BFDA) was an experimental material obtained from TRW Inc. The 2,2-bis[4(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF) and 3,5-diaminobenzotrifluoride (DABTF) were experimental monomers synthesized by Ethyl Corporation and NASA Langley Research Center, respectively. Kapton H film was obtained from duPont de N'emoirs and used for comparison. Figures 1(a) and 1(b) show the chemical structure of the dianhydride and diamine monomers investigated.

Polymer and Film Synthesis

Polyamic acid precursor solutions were prepared in closed vessels at ambient temperature by reacting stoichiometric amounts of diamine and dianhydride in dimethylacetamide at a concentration of 15-20% solids by weight. The resulting high viscosity polyamic acid solutions were cast onto glass plates in a dust-free chamber at a relative humidity of 10%. Solutions were spread with a doctor blade and gaps were set so as to produce a 25 μm thick film. The polyamic acid films were thermally converted to the corresponding polyimide films by heating in a forced air oven for one hour each at 100, 200 and 300 °C.



1(a)



1(b)

Figure 1. (a) Chemical structure of dianhydride monomers. (b) Chemical structure of diamine monomers.

Density and Dielectric Measurements

Densities were determined for the fully cured polyimide films in a density gradient tube prepared with aqueous $ZnCl_2$ solutions according to ASTM D1505-60T. Dielectric constants of the polyimide films were determined using a Hewlett Packard 8510 Automated Network Analyzer over the frequency range of 8-12 GHz. All films were desiccated in a heated vacuum oven prior to positron lifetime measurements.

Saturation Moisture Content Measurements

The samples were first desiccated by heating them to 120 °C in a vacuum oven till their weights became constant. They were then submerged in water at 90 °C till their weights stabilized. The saturation moisture content by weight was determined as (saturated sample weight- desiccated sample weight)/(desiccated sample weight). The saturation moisture fraction by volume was then calculated from the measured weight fraction as follows:

(Saturation Moisture Fraction by Volume)

$$= \frac{\rho(\text{Saturation Moisture Fraction by Weight})}{1 + \rho(\text{Saturation Moisture Fraction by Weight})}$$

where ρ is the density of the polymer sample.

Positron Lifetime Measurements

Positron lifetimes in the test films were measured using a recently developed low energy positron flux generation scheme (4). Briefly, the procedure involves the use of a thin aluminized mylar film as the positron source holder sandwiched between two well-annealed polycrystalline, high purity, tungsten moderator strips. The test films are introduced between the source holder and the moderator strips, thus serving an additional purpose of electrically insulating the source holder from the moderator strips. When a small negative potential ($-V$) is applied between the source holder and the moderator strips, the thermalized positrons diffusing out of the moderators are attracted to the source holder thus forcing them to enter and annihilate in the test films. A positive potential, ($+V$), on the other hand, forces the outdiffusing positrons back into the moderator strips. The difference between the positron lifetime spectra with the source at $\mp V$ volts with respect to the moderator strips is thus entirely due to the positrons annihilating in the test films. The lifetime data were acquired using a 250 microcuries Na^{22} positron source and a standard fast-fast coincidence measurement system with a time resolution of approximately 225 picoseconds. Attempts were made to analyze the lifetime spectra into 2- and 3-components using POSITRONFIT-EXTENDED (5) program. The best least squares fit to the data were obtained with 2-component analysis. Typical positron lifetime spectra are shown in Figure 2(a) and 2(b). It required about 6 hours to

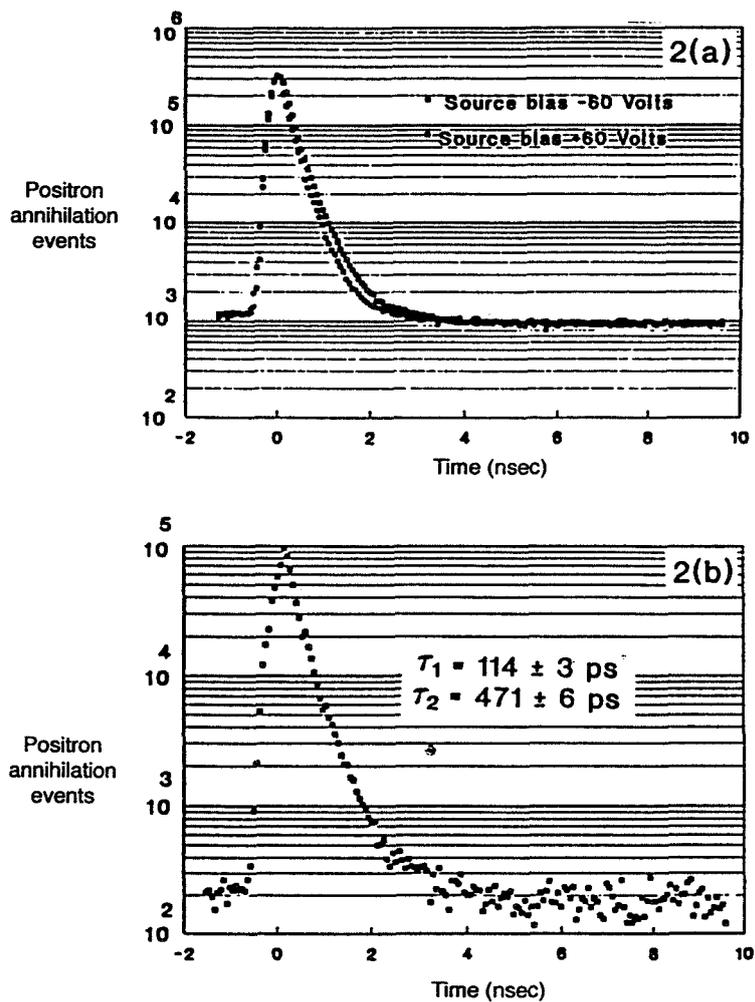


Figure 2. (a) Comparison between positive and negative source bias lifetime spectra in Kapton films. (b) Positron lifetime spectrum in Kapton films obtained by subtracting normalized positive bias spectrum from negative spectrum.

obtain 10^6 counts in the total spectrum in each case. The measurements were made at room temperature and ambient pressure.

RESULTS AND DISCUSSION

The physical and electrical properties of the films investigated are summarized in Table I. The positron lifetime component values, their respective intensities, and the microvoid volumes are summarized in Table II.

The longer positron lifetime in each test film corresponds to the positrons trapped in the potential defects (microvoids) in the test films. These microvoids result from fluctuations in the packing density of the macromolecular chains. The sizes of these microvoids are too small for the formation and localization of positronium atoms. However, free positrons can be trapped at these sites with subsequent annihilation. The radii of the microvoids (R) in nanometers and the trapped positron lifetime (τ_2) in nanoseconds are related as follows:

$$\frac{1}{2.5\tau_2} = \left(1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \frac{2\pi R}{R + \Delta R} \right) \quad (1)$$

where $\Delta R = 0.1659$ nanometers.

This equation differs from the conventional model (6) for positronium-forming media in having $1/2.5\tau$ instead of $1/2\tau$ as the left hand side term. This form has been dictated by the following considerations: (a) The positron annihilation in polyimides reportedly (7) differs considerably from that observed in most polymers. It proceeds from the free or trapped positron states without the formation of positronium atoms; (b) Positron lifetime spectra in all of the polyimides (PMDA, BFDA, BTDA and 6FDA-based polyimides etc.) investigated in this laboratory exhibit only two lifetime components. The shorter lifetime (τ_1) ranges from 100 to 300 picoseconds and arises from free positron

Table II. Positron Lifetimes and the Free Volume Fractions in the Test Films

Sample	Positron Lifetime values ^(*)		Microvoid	Free Volume
	τ_1/I_1 (ps/%)	τ_2/I_2 (ps/%)	Volume $V_f(\text{Å}^3)$	Fraction f(%)
Kapton (Ref)	$114 \pm 3/65.3 \pm 1.$	$471 \pm 6/34.7 \pm 1.$	1.54 ± 0.19	2.02 ± 0.27
BFDA + ODA	$223 \pm 4/73.2 \pm 1.$	$699 \pm 17/26.8 \pm 1.$	12.26 ± 1.10	12.43 ± 1.09
BFDA + 4-BDAF	$131 \pm 2/71.8 \pm 1.$	$790 \pm 12/28.2 \pm 1.$	18.36 ± 0.85	19.56 ± 0.91
6FDA + DDSO ₂	$170 \pm 3/72.5 \pm 1.$	$623 \pm 14/27.5 \pm 1.$	7.94 ± 0.75	8.26 ± 0.79
BFDA + DABTF	$135 \pm 4/68.6 \pm 1.$	$653 \pm 15/31.4 \pm 1.$	9.57 ± 0.96	11.41 ± 1.14
6FDA + APB	$254 \pm 4/86.2 \pm 1.$	$867 \pm 39/13.8 \pm 1.$	23.93 ± 2.83	12.5 ± 1.48
BTDA + ODA	$124 \pm 3/60.9 \pm 1.$	$531 \pm 7/39.1 \pm 1.$	3.7 ± 0.25	5.48 ± 0.37

(*) τ_1 and τ_2 are the lifetimes in picoseconds of positrons annihilating promptly and after trapping in microvoids, respectively. I_1 and I_2 are their respective intensities in percent.

annihilation. The longer lifetime (τ_2), whose value ranges from 400 to 900 picoseconds, has been reportedly (8, 9) associated with positrons trapped at defect sites (microvoids). Recently, Deng et al. (10) have reported that $1/2\tau_2$ for localized positronium can be paralleled by $1/n\tau_2$ for localized positrons for determining the microvoid radius. The maximum value of $1/n\tau_2$, which corresponds to the minimum radius of the free volume hole, is ≈ 1 . Thus for $\tau_2 \geq 0.4$ nanoseconds, $1/2.5\tau_2$ becomes the appropriate form. It implies that the radius of the smallest free volume hole (microvoid) in polyimides corresponds to a trapped positron lifetime of 400 picoseconds. The microvoid volume (V_f) is given by $4/3\pi R^3$. The free volume fractions in the test films were calculated as follows:

$$f = CI_2V_f \quad (2)$$

where C is a structural constant and I_2 is the intensity of the trapped positron lifetime component. The structural constant was calculated by equating the free volume fraction in Kapton with its saturation moisture fraction by volume. This is justifiable since Kapton has no hydrophobic atoms in its molecular structure. If, however, the space accessible to positrons is not identical to the volume accessible to water, the value of the structural constant C would be slightly different. It has been assumed that the structural constant C has the same value for all of polyimide films tested. The free volume fractions of all the films tested are summarized in Table II.

Even though the chemical structures of the films investigated are not identical, their polarizabilities are not expected to be significantly different. Recently, Misra et al. (11) have reported similar conclusions about the effects of fluorine substitutions on the dielectric constants of similar aromatic polyimides. Thus, the differences in the dielectric constants are expected to arise mainly from the differences in the free volume fractions of the films studied. The effect of free volume fraction (f) on the dielectric constant (ϵ) of the films can be calculated as follows. As illustrated in Figure 3, the aggregate of the free volume cells in the film of thickness d can be represented by an empty (air) strip of thickness df . The effect of the air strip on the dielectric constant of the film can be calculated by considering a parallel plate condenser with the test film as its dielectric medium. The dielectric medium is thus made up of a resin strip of thickness of $d(1-f)$ and an airstrip of thickness df in series. The capacitance (C) of such a parallel plate condenser can be written as:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (3)$$

where $C = \epsilon(A/4\pi d)$

$C_1 = \epsilon_R(A/4\pi d(1-f))$

$C_2 = \epsilon_{Air}(A/4\pi df)$

and A = Area of the condenser plates.

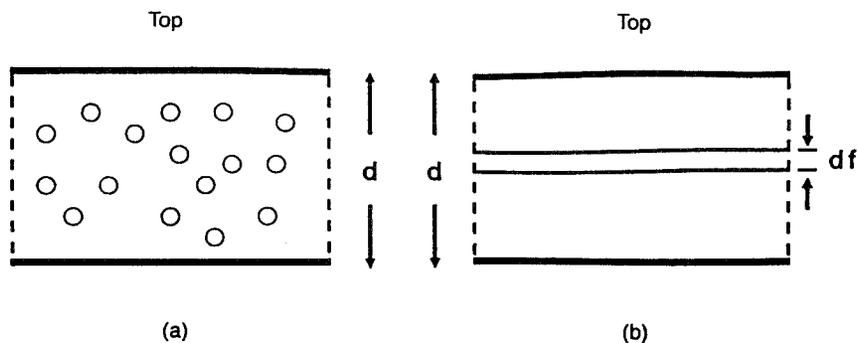


Figure 3. Cross sectional view of the test film. (a) Randomly distributed free volume cells. (b) Equivalent free volume strip.

Substituting the values of C , C_1 , and C_2 in equation 3, we obtain:

$$\frac{1}{\epsilon} = \frac{1-f}{\epsilon_R} + \frac{f}{\epsilon_{Air}} \quad (4)$$

The value of ϵ_R , which corresponds to the value of ϵ for zero free volume fraction, was obtained from the ϵ vs f data illustrated in Figure 4 and has been found to be 3.55. It should be emphasized that $\epsilon_R = 3.55$ is the predicted value of the dielectric constant of a free-volume-hole-free polyimide film. This value should not be compared with experimental values of ϵ_R for any polyimide film unless it is known to have zero free volume fraction. Furthermore, if the saturation moisture content of Kapton is not equal to its free volume fraction, the value of ϵ may be slightly different. The measured and calculated values of the dielectric constants for various test films are summarized in Table III and illustrated in Figure 5. It is noted that the test samples with the largest free volume fractions have the lowest values of dielectric constants as suggested by equation 4. The large free volumes in these samples are due to the presence of meta linkages and bulky CF_3 in their molecular architecture. A comparison of the saturation moisture data in Table I and the free volume fraction values in Table II shows that the saturation moisture fractions are much less than the free volume fractions in all samples, except Kapton in which they have been assumed to be equal. This is presumably the result of hydrophobicity of fluorine atoms present in high concentration in the backbones of the test samples other than Kapton.

CONCLUSIONS

Positron lifetime spectroscopy provides a sensitive technique for characterizing

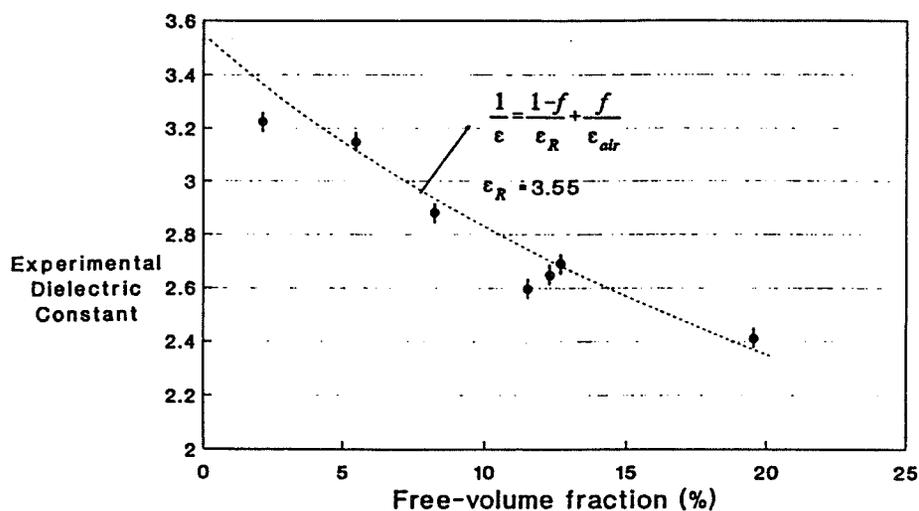


Figure 4. Experimental dielectric constant vs. free-volume fraction.

Table III. Comparison Between the Experimental and Calculated Values of the Dielectric Constants

Sample	f(%)	ϵ (Expt)	ϵ (calc)
Kapton (Ref)	2.02 ± 0.27	3.20 ± 0.03	3.31 ± 0.03
BFDA + ODA	12.43 ± 1.09	2.63 ± 0.03	2.69 ± 0.05
BFDA + 4-BDAF	19.56 ± 0.91	2.44 ± 0.03	2.37 ± 0.04
6FDA + DDSO ₂	8.26 ± 0.79	2.86 ± 0.03	2.93 ± 0.05
BFDA + DABTF	11.41 ± 1.14	2.55 ± 0.03	2.74 ± 0.06
6FDA + APB	12.5 ± 1.48	2.71 ± 0.03	2.70 ± 0.07
BTDA + ODA	5.48 ± 0.37	3.15 ± 0.03	3.12 ± 0.03

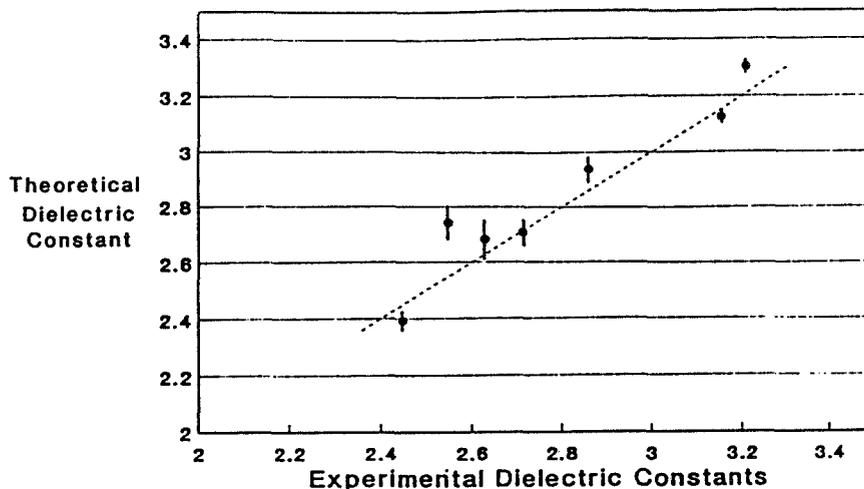


Figure 5. Comparison between the experimental and theoretical dielectric constants.

thin polymer films in terms of their free volumes and dielectric constants. When combined with saturation moisture determination, it also provides useful information about their moisture susceptibility. It is apparent that the presence of fluorine atoms in the polymer architecture reduces their moisture pick up, and hence the moisture-induced degradation in their physical and electrical properties. Also, the bulky CF_3 groups and meta linkages in their structure enhance their inter-molecular spacing resulting in higher free volume fraction and, consequently, lower dielectric constant.

REFERENCES

1. St. Clair, A. K.; St. Clair, T. L., U.S. Patent 4,603,061, 1986.
2. Stoakley, D. M.; St. Clair, A. K. *Proc. of the Mat. Res. Soc. Symp.*, 1991, 131-136.
3. St. Clair, A. K.; St. Clair, T. L.; Winfree, W. P. *Proc. of the ACS Division of PMS & E.* 1988, 59, 28.
4. Singh, J. J.; Eftekhari, A.; St. Clair, T. L. *Nucl. Instrum. Methods. Phys. Res.*, 1991, B53, 342-348.
5. Kirkegaard, P. *Comput. Phys. Commun.*, 1974, 7(7), 401-409.
6. Nakanishi, H.; Wang, S. J.; Jean, Y. C. *Proc. Int'l Symp. on Positron Annihilation Studies of Fluids.* 1988, 292-298.
7. Askadskii, A. A.; Tushin, S. A.; Kazantseva, V. V.; Kovrins, O. V. *Polymer Science U.S.S.R.*, 1990, 32 (No. 12) 2560-2568.
8. Hautojarvi, P.; Vehanen, A. In *Positrons in Solids*; Hautojarvi, P., Ed.; Springer-Verlag: New York, 1979; pp 1-23.

9. Stevens, J. R. In *Methods of Experimental Physics*; Fava, R. A. Ed.; Academic Press: New York, 1980; Vol. 16 (Part A) pp 371-403.
10. Deng, Q.; Sundar, C. S.; Jean, Y. C. *J. Phys. Chem.*, 1992, 96, 492-495.
11. Misra, A. C.; Tesoro, G.; Hougham, G.; Pendharkar, S. M. *Polymer*, 1992, 33, 1078-1082.

RECEIVED December 30, 1992

Reprinted from ACS Symposium Series No. 537
Polymers for Microelectronics Resists and Dielectrics
Larry F. Thompson, C. Grant Wilson and Seiichi Tagawa, Editors
Copyright © 1994 by the American Chemical Society
Reprinted by permission of the copyright owner

Appendix 7

"Positron Lifetime Spectroscopy for Investigation of thin Polymer Coatings" Jag. J. Singh, Abe Eftekhari and Danny R. Sprinkle, NASA Tech, Memo 4421 Feb. (1993).