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A STUDY OF PHYSICAL PROPERTIES OF ODPA-p-PDA POLYIMIDE FILMS

JAG J. SINGH, ABE EFTEKHARI, AND TERRY L. ST. CLAIR

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Langley Research Center
Hampton, Virginia 23665-5225

A Study of Physical Properties of ODPA-p-PDA Polyimide Films

By

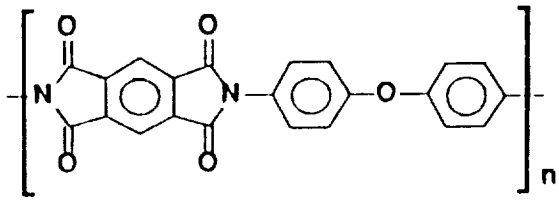
Jag J. Singh, Abe Eftekhari, and Terry L. St. Clair

INTRODUCTION

As a part of continuing research on structure-property relationships in polyimides, we have been studying the properties of PMDA/ODA and ODPA-p-PDA (isomeric polymers) and their mixtures. These studies have indicated that the properties of blends and copolymers incorporating these isomers are not just the sum of their constituents. To begin with, both PMDA-ODA and ODPA-p-PDA are semi-crystalline, whereas their blends and copolymers have considerably less crystallinity. The saturation moisture content of the blends and copolymers are considerably higher than those of the constituent isomers. It was discovered that ODPA-p-PDA isomer had the lowest saturation moisture content, even though it has the largest size microvoids. This novel property of ODPA-p-PDA prompted us to study this polyimide in detail, including its lower molecular weight versions with phthalimide endcaps. The results of these studies are described in the following sections.

Polymer Preparation

The polymer that is the subject of this study is an isomeric form of the commercial polyimide film Kapton*. The chemical structure of Kapton* is

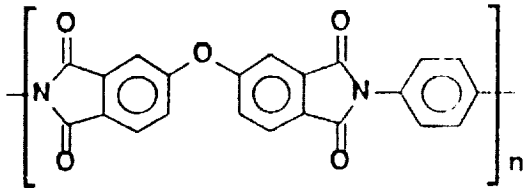


PMDA/ODA

where PMDA/ODA are acronyms for pyromellitic dianhydride/oxydianiline, the two monomers from which it is prepared.

The isomeric form of PMDA/ODA in this study has the following chemical structure:

*Kapton is a registered trademark of DuPont.



ODPA/p-PDA

where ODPA/p-PDA are acronyms for oxydiphthalic anhydride/ p-phenylenediamine. The ODPA monomer was purchased from OxyChem and was used as received. The p-PDA was a maximum purity monomer that was used as received from Fluka. Phthalic anhydride (Eastman) was utilized as an endcap when stoichiometry was offset in favor of the p-PDA.

All polymers were prepared at 15% solids in N, N-dimethylacetamide (DMAc) at room temperature. Molar offsets in stoichiometries (excess p-PDA) were made at 0.5, 1.0, and 2.0% in order to systematically lower the molecular weight of the ODPA/p-PDA. The excess amine groups that resulted due to the offset were reacted with phthalic anhydride in order to prevent chain extension reaction during film preparation. Inherent viscosities were determined at 0.5% solids in DMAc at 35 ^{o}C.

Films were prepared by doctoring the viscous polymer solutions onto sodalime plate glass, allowing the films to dry overnight in a nitrogen-purged box to a tack-free form, and curing them 1 hour each at 100, 200, and 300 ^{o}C, successively. The cured films were removed from the glass plates by immersing them in hot water.

Experimental Procedure

The major parameter of interest in the present study has been the free volume fraction in the test polyimide samples since all physical properties are ostensibly related to it. If the entry of water in the test material is entirely physical, the free volume can be calculated from a measurement of its saturation moisture content. However, this is not always the case. Sometimes the invading water molecules get adsorbed in the surface states or attach to the chemical backbone of the polymers, thereby further impacting their physical characteristics.

We have developed[1-3] a Positron Annihilation Spectroscopy (PAS) technique for measuring the free volume cell size and total free volume fraction in polymer materials. It involves the injection of energetic positrons in the test sample. The incident positrons are quickly thermalized. After thermalization, they may either annihilate as free positrons or be trapped in defects/microvoids before eventual annihilation. In the latter case, the positrons may form positronium (Ps) atoms before annihilation with the surrounding electrons. The lifetime of the Ps atoms is a very strong function[4-5] of the physical size of the microvoids (V_f):

$$1/2\tau = (1-R/R_o + A \text{ Sin } 2\pi R/R_o) \quad (1)$$

where τ = Ps lifetime in nanoseconds

$R_o = R + 0.1656$ in nanometers and

A is constant ($\frac{1}{2\pi} \rightarrow 1$).

The microvoid volume (V_f) is given by $4/3\pi R^3$. In the present study, we find that the experimental results are more consistently explained if $A = 1/\pi$.

It is anticipated that the dielectric constant of the test polymers will be intimately related to their free volume. For example, if the free volume fraction in the dry test polymer is f^*, its dielectric constant ε is given by:

$$1/\varepsilon = (1-f)/\varepsilon_R + f/\varepsilon_C \quad (2)$$

where ε_R is dielectric constant of the resin and ε_C is the dielectric constant of the medium inside the free volume cell ($\varepsilon_C = 1$ for dry sample and 80 for sample saturated with water). Thus a measurement of dielectric constant under various experimental conditions should also provide useful information about free volume and vice versa.

EXPERIMENTAL RESULTS AND DISCUSSION

The first phase of this study involved investigation of physical properties of PMDA/ODA and OPDA-p-PDA isomers and their mixtures. Table 1 summarizes their saturation moisture contents as well as positron lifetime data. These results are illustrated in figure 1.

From these data, it is evident that ODPA-p-PDA has the lowest saturation moisture content and should therefore be most appropriate for aerospace applications. It was therefore decided to examine the behavior of ODPA-p-PDA films in detail, including different molecular weight versions which have stoichiometries offset to lower molecular weight. The results of positron lifetime measurements in various forms of ODPA-p-PDA films are summarized in Table II and illustrated in figure 2.

(*) f can be obtained using the following relations[6]:

$$f = C \; I \; V_f \quad (3)$$

where C is constant, I is intensity of the longest component in the positron lifetime spectrum.

From the data summarized in Table II, it is noted that a significant morphological change occurs at 1% offset level. The microvoid size goes down by almost a factor of 2 compared with its value at 0.5% offset. It will be intriguing to explore if there is a possible correlation between free volume cell size (V_f) and the number average molecular weight (M) of the polymer film. It is well known that the viscosity (η) and the number average molecular weight (M) of the polymers in solution are related by the Mark-Houwink relation[7]:

$$\eta = a\ (M)^b \qquad (4)$$

Following the arguments given by Flory et al[8], we can expect a similar relation between V_f and M, i.e.,

$$V_f = a'\ (M)^{b'} \qquad (5)$$

Using the M-values from M-H relation, we obtained initial estimates of constants a' and b' in equation 5. These estimates were then used as initial inputs to obtain their final values by minimizing the differences between M-H values and our prediction for the molecular weights. The M-values for these films have also been calculated using statistical analysis of the effects of offsetting stoichiometries. The comparison between the M- values calculated using M-H expression, statistical analysis, and our expression (equation 5) are summarized in Table III and illustrated in figure 3. It is apparent that the statistical analysis results are closer to our values than the predictions of the M-H equation.

A natural corollary of the above arguments will be to check if there is any relationship between the dielectric constant and the free volume fraction in the test films. We have measured the dielectric constant values of these films using a standard parallel-plate condenser bridge technique at 1 MHz. These results are summarized in Tables IV and V.

Table V summarizes the comparison between the ε(experimental) and ε(calculated) values for these samples. These results are illustrated in figure 4. Clearly, the agreement is quite good, supporting the essential accuracy of the physical model.

Another feature of interest in these films is their saturation moisture content. These values were measured using the standard procedure of immersing them in hot distilled water till their weights became constant. These measurements are summarized in Table VI. Also included in this table are the free volume fractions determined from positron lifetime values in these samples. Figure 5 illustrates these results.

It is obvious that the saturation moisture level (V/O) is higher than the microvoid volume fraction determined by PAS technique. This suggests that part of the moisture (water) may be adsorbed in the

surface states. This fraction appears to increase as the molecular weight decreases.

CONCLUDING REMARKS

On the basis of the data discussed in the preceding pages, several interesting deductions can be made: (1) The average microvoid size in polyimides is strongly related to their molecular weight. Similarity of the relations between (η vs. M) and (V_f vs. M) indicates that the viscosity of the polymer solution and free volume cell size in the solid phase are intimately related to the chain dynamics; (2) as the free volume in the test sample decreases its molecular weight also decreases; and (3) the dielectric constants of the polyimide samples are intimately related to their molecular architecture, i.e., their free volume fractions impact their dielectric constants strongly. Of these three findings, the first one constitutes a major achievement since it enables us to estimate the molecular weight of an intractable polymer in solid state.

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TABLE I

Summary of Saturation Moisture Values and Positron Lifetime Data

No.	Sample	Saturation Moisture Content	Lifetime/Intensity
1	PMDA-ODA	3.2 Weight %	535 ps/32%
2	ODPA-p-PDA	1.79 Weight %	849 ps/19%
3	PMDA-ODA/ODPA-p-PDA (Blend)	3.97 Weight %	472 ps/22%
4	PMDA-ODA/ODPA-p-PDA (Copolymer)	3.61 Weight %	436 ps/39%

TABLE II

Summary of Positron Lifetime Data in Various Molecular Weight Forms of ODPA-p-PDA

No.	Sample	Positron Lifetime Data	
		τ/I	V_f (Calculated From τ/I)
1	ODPA-p-PDA (Ref.)	849 ps/19%	14.6 A^3
2	ODPA-p-PDA (0.5% Offset)	815 ps/16%	10.8 A^3
3	ODPA-p-PDA (1.0% Offset)	619 ps/28%	5.5 A^3
4	ODPA-p-PDA (2.0% Offset)	523 ps/34%	2.5 A^3

TABLE III

Comparison Betweeen M-Values Calculated by Various Methods

No.		$\eta^{(+)}$ (dl/gm)	$M^{(++)}$	V_f (A^3)	$M^{(*)}$	$M(Cal.)^{(**)}$
1	ODPA-p-PDA (Ref.)	1.3	88000	14.6	88399	(80 - 100) x1000
2	ODPA-p-PDA (0.5% Offset)	0.5	18000	10.8	60208	76400
3	ODPA-p-PDA (1% Offset)	0.4	13000	5.5	25585	38200
4	ODPA-p-PDA	0.35	10000	2.54	9591	19100

(+) These values were obtained by using Cannon-Fenske viscometer at 0.5 gm/dl concentration in N, N-dimethylacetamide (DMAc) at 35 °C (see page 2).

(++) These values have been calculated from[9]

$$\eta = 1.4 \times 10^{-3} (M)^{0.6} \quad (4A)$$

(*) These values have been calculated from:

$$V_f = 1.86 \times 10^{-3} (M)^{0.787} \quad (5A)$$

(**) These values have been calculated using the following equation:

$$\text{Degree of Polymerization (N)} = 1/(1-p) \quad (5B)$$

where p is the stiochiometry after the offset

$$M(Cal) = 382\ N \quad (5C)$$

(A good approximation for p = 0 is 80,000 - 100,000 Amu)

TABLE IV

Summary of Dielectric Constant Values
of the Test Films

No.	Sample	Thickness (Nominal, mills)	Dielectric Constant (ε) (Dry Sample)
1	ODPA-p-PDA (Ref)	1.68	2.62 ± 0.02
2	ODPA-p-PDA (0.5% Offset)	1.36	2.91 ± 0.02
3	ODPA-p-PDA (1.0% Offset)	1.44	2.97 ± 0.02
4	ODPA-p-PDA (2.0% Offset)	2.06	2.99 ± 0.02

TABLE V

Comparison Between the Experimental and Calculated
Values of Dielectric Constants

No.	Sample	ε(Dry) Experimental	ε(Dry) Calculated
1	ODPA-p-PDA (Ref)	2.62 ± 0.02	2.62 ± 0.02
2	ODPA-p-PDA (0.5% Offset)	2.91 ± 0.02	2.85 ± 0.02
3	ODPA-p-PDA (1.0% Offset)	2.97 ± 0.02	2.92 ± 0.02
4	ODPA-p-PDA (2.0% Offset)	$2.99 \pm 0.02^{(*)}$	$3.00 \pm 0.02^{(**)}$

$^{(*)}$This value was calculated from ε(ambient) (50% saturation) using equation 2.

$^{(**)}$This value was calculated from ε(saturated) using equation 2.

TABLE VI

Summary of Saturation Moisture Content of the Test Films

No.	Sample	Saturation Moisture Content (Weight)	(Volume)	Free Volume Fraction From PAS Study (*) (f %)
1	ODPA-p-PDA (Ref)	1.79	2.57	2.57
2	ODPA-p-PDA (0.5% Offset)	1.86	2.63	1.96
3	ODPA-p-PDA (1.0% Offset)	1.77	2.54	1.43
4	ODPA-p-PDA (2.0% Offset)	1.61	2.32	0.80

(*) These values were obtained using the equation 3:

$$f = C\ I\ V_f$$

The constant C was obtained by equating f with the saturation moisture content (V/O) in the ODPA-p-PDA (Reference) sample, i.e.,

$$0.0257 = C\ (19)\ V_f$$
$$= C\ (19)\ (4/3\ \pi\ R^3)$$
$$= C\ (19)\ (14.6)$$
$$(10793)^{-1} = C$$

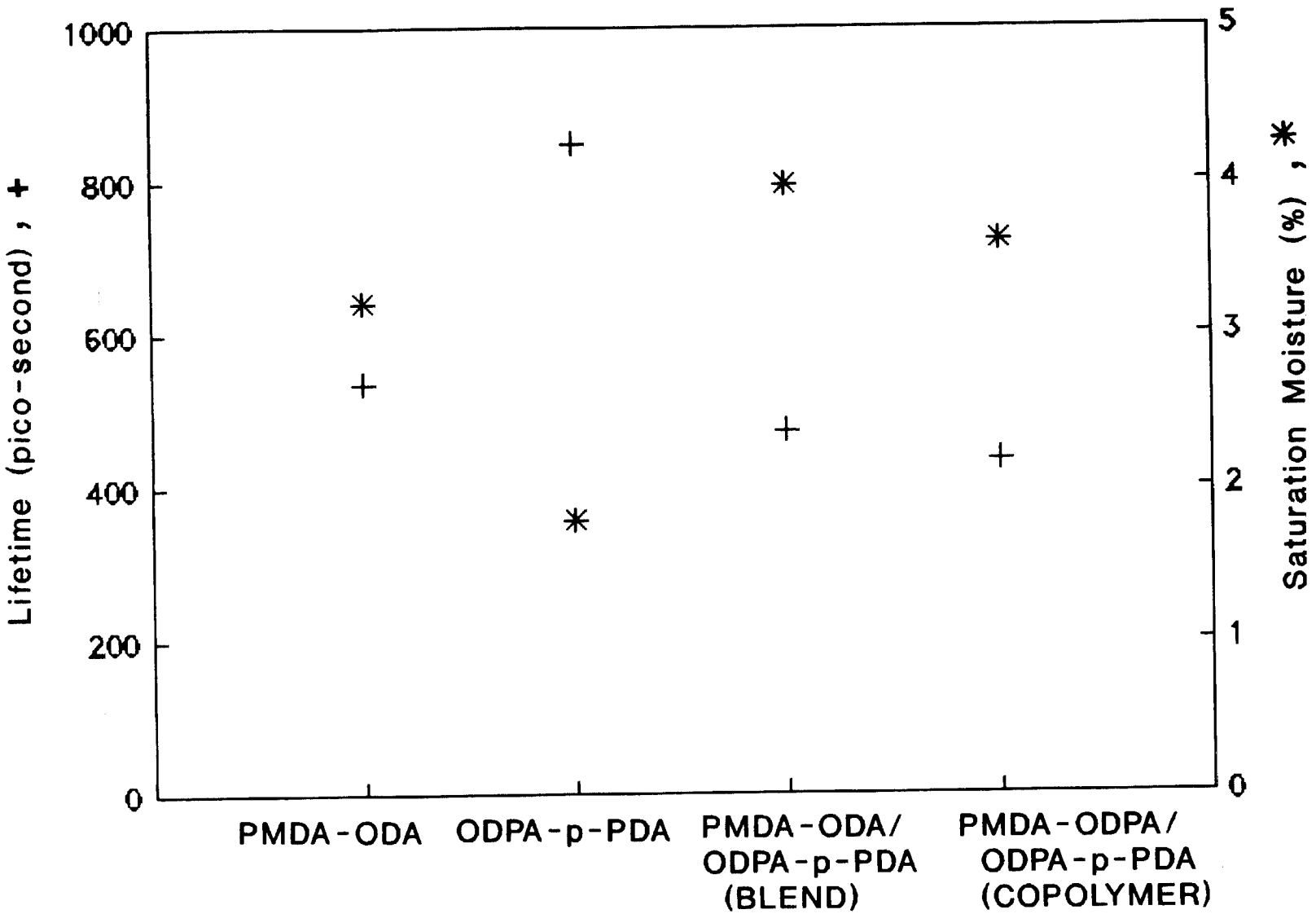

Figure 1. Moisture content & Lifetime measurements in PMDA-ODPA, OPDA-p-PDA isomers and their mixture.

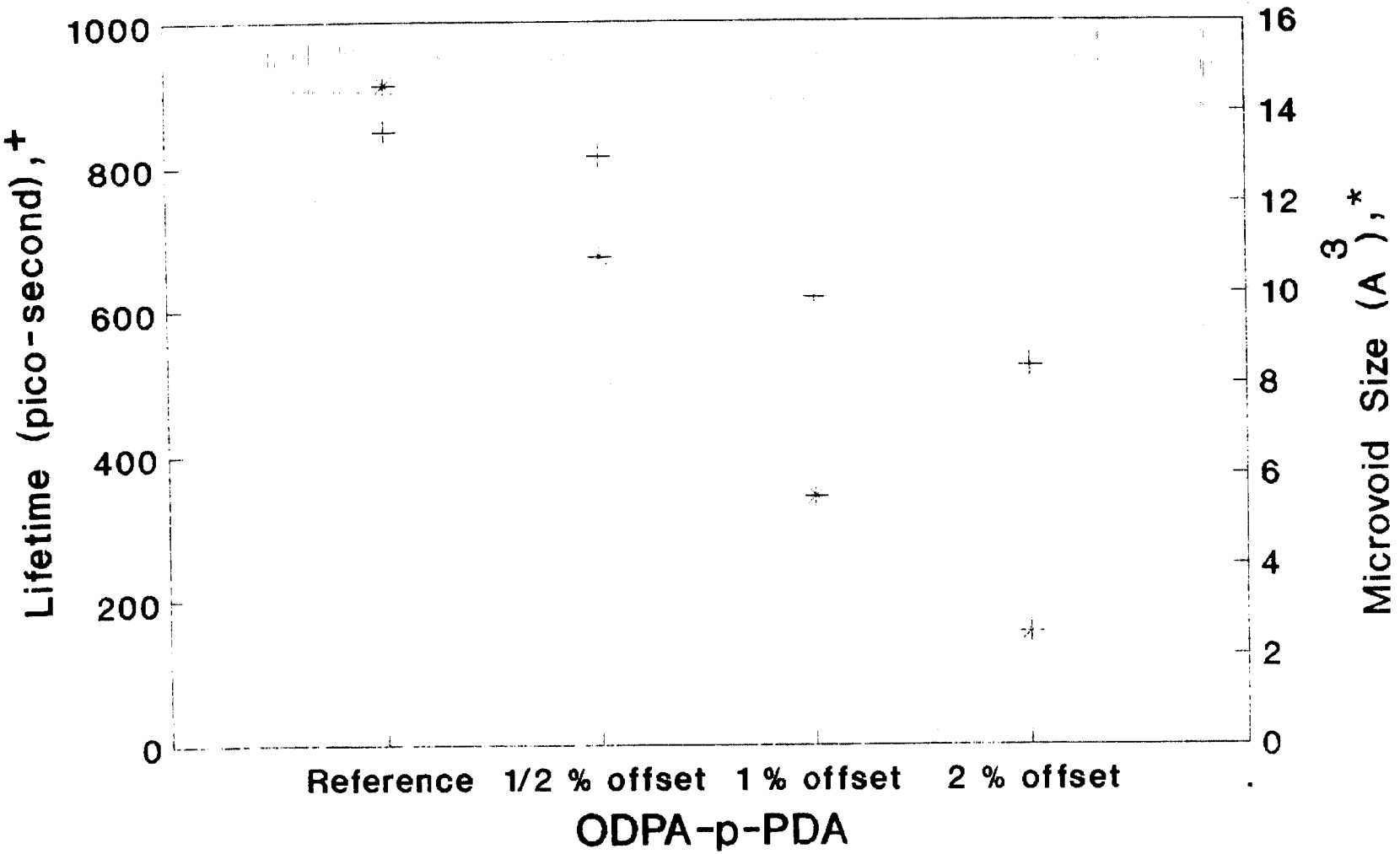

Figure 2. Positron Lifetime date in ODPA-p-PDA with different degrees of stoichiometry offset.

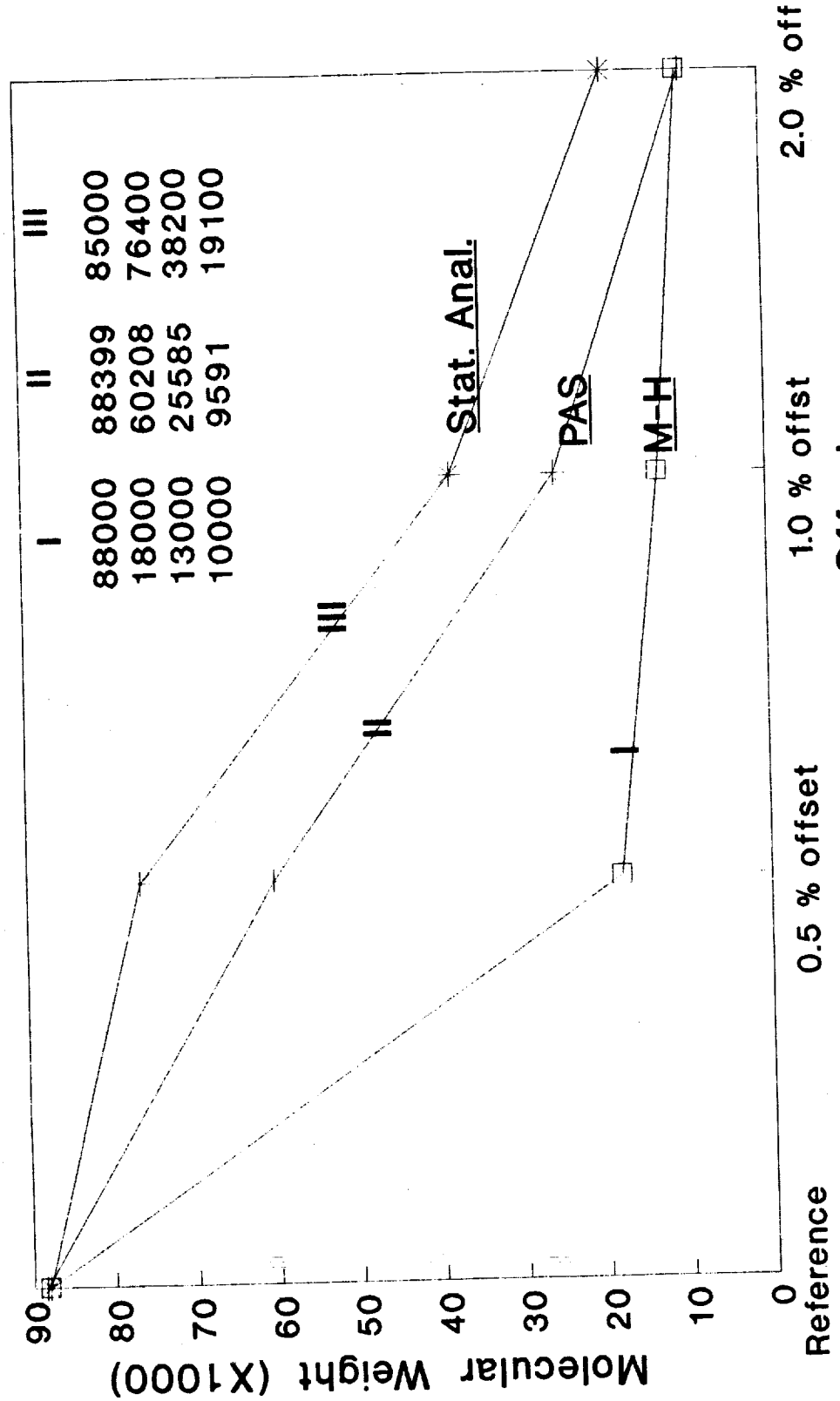

Figure 3. Comparison Between calculated molecular weights of ODPA-p-PDA films from M-H expression, PAS method, and Statistical calculation.

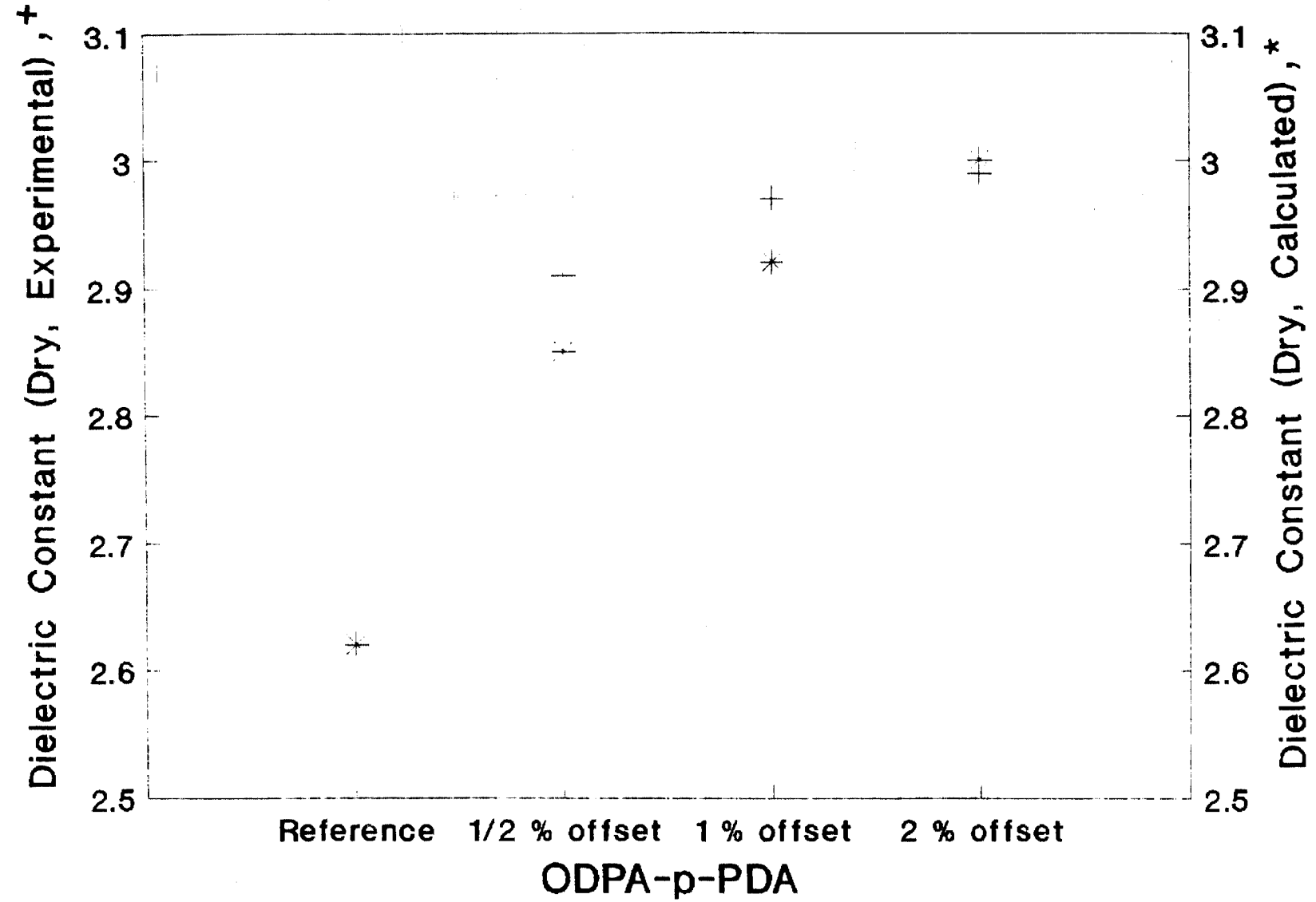

Figure 4. Comparison between calculated and experimental dielectric constants for ODPA-p-PDA films.

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Jag J. Singh and Terry L. St. Clair: Langley Research Center, Hampton, Virginia.
Abe Eftekhari: Analytical Services and Materials, Inc., Hampton, Virginia.

16. Abstract

We have investigated physical properties of ODPA-p-PDA polyimide films, including their lower molecular weight versions with phthalimide endcaps. Free volume, determined by low energy positron annihilation in the test films, was the major parameter of interest since all other physical properties are ostensibly related to it. It affects the dielectric constant as well as the saturation moisture pickup of the test films. We also developed an empirical relation between the free volume and molecular weight of the test films, comparable to the Mark-Houwink relation between the polymer solution viscosity and the molecular weight. Development of such a relation constitutes a unique achievement since it enables researchers to estimate the molecular weight of an intractable polymer in solid state for the first time.

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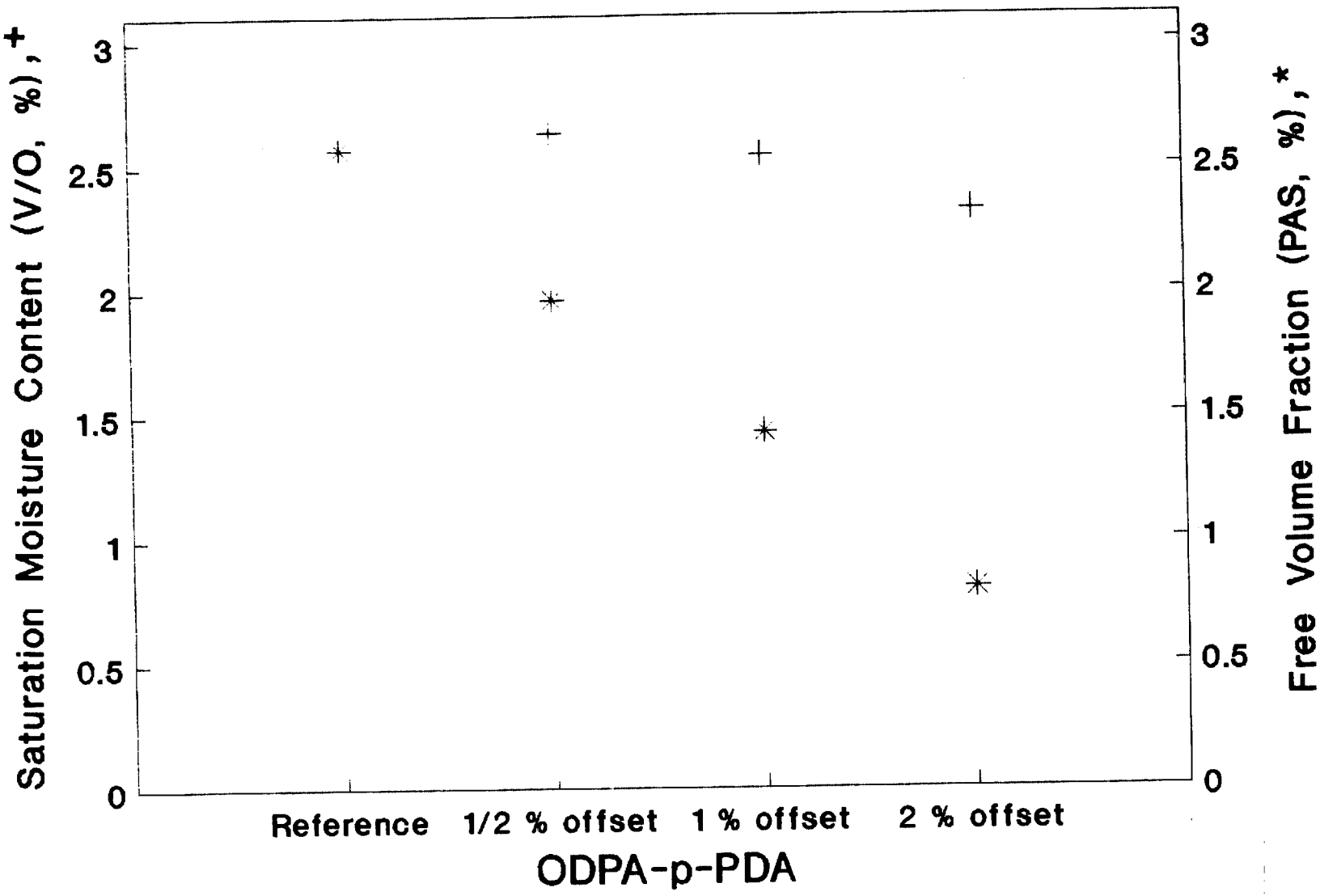

Figure 5. Comparison between the saturation moisture content and free volume fraction for ODPA-p-PDA films.