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Influence of Free Volume Change on the Relative Permittivity and Refractive Index in Fluoropolyimides

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ABSTRACT: The often observed decrease in relative permittivity (ϵ') and refractive index (n) that accompanies fluorine substitution is the result of several effects. Fluorine replacement for hydrogen is known to decrease local electronic polarization and is thought to frequently increase fractional free volume. Both of these effects can independently decrease ϵ' and n, and this paper attempts to assign the observed decreases between these mechanisms for a series of hydrogen/fluorine polyimide analogs.

Introduction

This paper attempts to determine the contribution of changes in free volume, which occur concomitantly with fluorine substitution, to the observed decreases in dielectric constant and the related refractive index. An analytical approach is introduced, and some intriguing preliminary results are reported.

The incorporation of fluorine can affect the dielectric constant in several ways simultaneously. Increases in free volume, which often accompany fluorine substitution, may decrease the dielectric constant by reducing the number of polarizable groups in a unit volume. Increases in free volume can be attributed to the greater steric volume of fluorine relative to hydrogen, which may interfere with efficient chain packing. In addition, the significant mutual repulsion of fluorine atoms on different chains, and the often-lower degree of polymerization, may influence the free volume. A correlation of high free volume with low dielectric constant has previously been found in polyimides.[1,2]

Furthermore, the electronic polarization is always lowered with fluorine substitution because of the smaller electronic polarizability of the C−F bond relative to C−H. In cases where fluorine is positioned nonsymmetrically, an increase in the dipole moment would result that could lead to substantial increases in the dipole orientation polarizability at low frequencies, thereby increasing the low-frequency dielectric constant[3].

Greater fluorine content also increases the hydrophobicity of the polymer. The diminished moisture content that results decreases the bulk dielectric constant at lower frequencies.

The influence of fluorine on the dielectric constant is thus a complex matter, and the net effect of the often conflicting dielectric consequences of fluorine substitution is not always readily predictable.

Experimental Section

The series of polymers utilized in this work are shown in Figure 1. All polyimides used are based on hexafluoroisopropylidene bis(phthalic anhydride) (6FDA). The structure of the diamine was varied. The synthesis of these materials is described elsewhere.[4−8]

The density of the polymer films was determined by either gradient pycnometer or density gradient column techniques. The refractive index was measured by a prism coupling method (Metricon) at 632.8 nm. Both in-plane, n_{TE}, and out-of-plane, n_{TM}, refractive indexes were measured and were used to compute the three-dimensional average refractive index as defined in eq 1. The dielectric constant was calculated with Maxwell's identity, shown in eq 2. In this work, the main

$$n = (2n_{\mathrm{TE}} + n_{\mathrm{TM}})/3 \qquad (1)$$

$$\epsilon' = n^2 \qquad (2)$$

objective was to attempt to separate two phenomena that occur simultaneously upon fluorine substitution: the decrease in the electronic polarizability and the increase in free volume. In order to do this, we normalized the experimental dielectric constants of hydrogen/fluorine analogs to values that would be predicted if the free volumes were identical. This was done utilizing the Clausius−Mossotti/Lorenz−Lorentz model (CM/LL) of dielectric mixing.

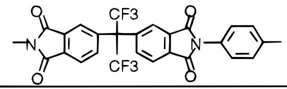
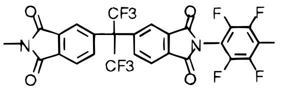
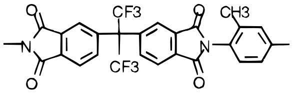
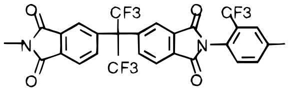
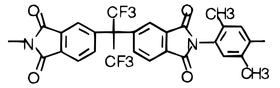
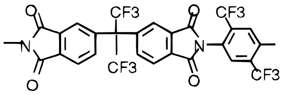
Polymer	Structure
6FDA-PDA	
6FDA-TFPDA	
6FDA-DAT	
6FDA-TFMPDA	
6FDA-2DAT	
6FDA-2TFMPDA	

Figure 1. Chemical repeat unit structures of polyimides.

Many methods have been employed to estimate the fractional free volume (VFF) in polymers. Positron annihilation measurements have been extensively used,[1,2,9,10] and computer simulation has been explored by us and others. The method used here was the group additivity technique popularized by Bondi and widely applied for a number of different purposes.[11−16]

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This was carried out by estimating the van der Waals or "occupied" volume, using group additivity tables and subtracting it from the molar volume (M/ρ), which is the total volume taken up by 1 mol of repeat units, including free and occupied volume. The fractional free volume is then given by

$$\mathrm{VFF} = \frac{(M/\rho) - \mathrm{VDW}}{M/\rho} \tag{3}$$

where M is the formula weight of a polymer repeat unit, ρ is the measured density, and VDW is the estimated van der Waals volume.

To normalize a dielectric constant to a value it would be predicted to have if the fractional free volume were changed, we utilize a model describing how the dielectric constant changes as different amounts of two substances with different dielectric constants are mixed. We will consider the "pure" polymer—that is, the van der Waals occupied part of the polymer only—to constitute one component, and we will consider the free volume to be a second component. We know the dielectric constant of free space to be 1.0. We need only to find the dielectric constant of the pure polymer (ϵ'_{vdw}) for each material to be able to then predict the ϵ' at any free volume state.

The CM/LL model has been used successfully to model isotropic mixtures of nonpolar liquids[17,18] and has also been used to model the dielectric behavior of polyimides with varying amounts of absorbed water.[19]

The CM/LL model takes the following form as a mixing equation:

$$\frac{\epsilon'_{\mathrm{mix}} - 1}{\epsilon'_{\mathrm{mix}} + 2} = \sum_i \theta_i \frac{\epsilon'_i - 1}{\epsilon'_i + 2} \tag{4}$$

Here, θ_i is the volume fraction of each component, and ϵ'_i is the dielectric constant of the pure components. For a two-component mixture consisting of free space and van der Waals volume, this expands to the following:

$$\frac{(\epsilon'_{\mathrm{mix}} - 1)}{(\epsilon'_{\mathrm{mix}} + 2)} = (\mathrm{VFF})\frac{(\epsilon'_{\mathrm{air}} - 1)}{(\epsilon'_{\mathrm{air}} + 2)} + (1 - \mathrm{VFF})\frac{(\epsilon'_{\mathrm{vdw}} - 1)}{(\epsilon'_{\mathrm{vdw}} + 2)} \tag{5}$$

The dielectric constant of free space, ϵ'_{air}, is known. The dielectric constant of one particular mix—that comprising the experimental sample, ϵ'_{exp}—is known. The experimental fractional free volume of the sample, $\mathrm{VFF}_{\mathrm{exp}}$, is estimated. This then becomes the following, from which ϵ'_{vdw} is easily solved:

$$\frac{(\epsilon'_{\mathrm{exp}} - 1)}{(\epsilon'_{\mathrm{exp}} + 2)} = 0 + (1 - \mathrm{VFF}_{\mathrm{exp}})\frac{(\epsilon'_{\mathrm{vdw}} - 1)}{(\epsilon'_{\mathrm{vdw}} + 2)} \tag{6}$$

Once we have obtained a value for ϵ'_{vdw}, we can substitute it back into the original form and obtain a predicted dielectric constant, ϵ'_{mix}, for any fractional free volume desired.

$$\frac{(\epsilon'_{\mathrm{mix}} - 1)}{(\epsilon'_{\mathrm{mix}} + 2)} = (1 - \mathrm{VFF})\frac{(\epsilon'_{\mathrm{vdw}} - 1)}{(\epsilon'_{\mathrm{vdw}} + 2)} \tag{7}$$

The variation of ϵ' with VFF is shown in Figure 2 for the single polymer 6FDA−PDA.

Results and Discussion

Polymer pairs such as 6FDA−PDA and 6FDA−TFPDA, which differ only in fluorine substitution, are considered. Using the measured dielectric constants (n^2) and the estimated fractional free volume, the dielectric constants for each material of a pair are normalized with the CM/LL model to the value they would be predicted to have at a fractional free volume that is intermediate between their two respective experimental VFF values.

Figure 3 shows the experimental (ϵ', VFF) points for both materials of a pair, superimposed on their CM/LL curves that predict how the ϵ' would change with a change in VFF. To normalize, the 6FDA−PDA ϵ' data point is shifted along its CM/LL curve to the intermediate VFF of 0.3784, and the 6FDA−TFPDA ϵ' data point is shifted along its CM/LL curve to the same intermediate VFF. The difference in the resulting normalized dielectric constants is an estimate of the change in dielectric constant due to differences in polarizability only. The complementary difference in ϵ' between the two materials ($\Delta\epsilon'_{\mathrm{exp}} - \Delta\epsilon'_{\mathrm{norm}} = \Delta\epsilon'_{\mathrm{VFF}}$) is the change in dielectric constant due solely to free volume changes. This value divided by the difference in the experimental dielectric constants gives the fraction of the observed decrease in ϵ' due to free volume changes.

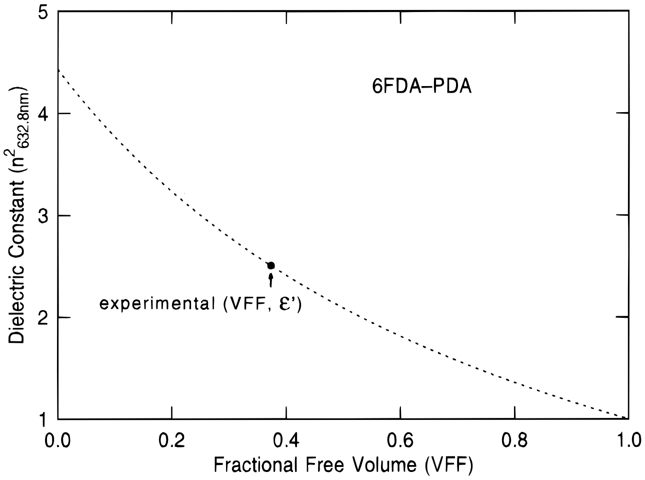

Figure 2. Predicted variation of ϵ' with VFF for 6FDA−PDA using the CM/LL model.

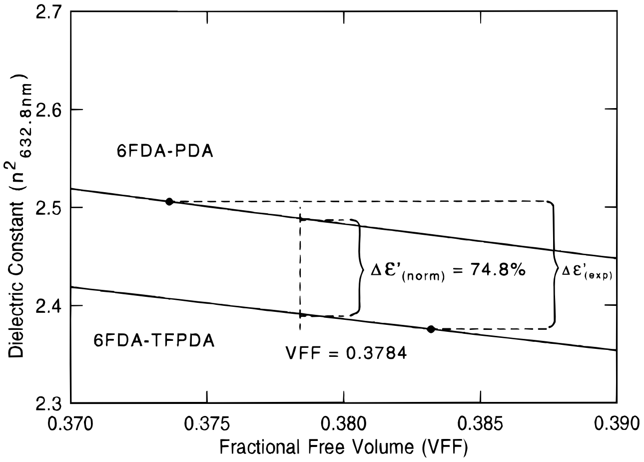

Figure 3. An example pair. Data points for 6FDA−PDA and 6FDA−TFPDA witH CM/LL curves. The normalization process is illustrated.

$$\%\Delta(n^2) \text{ due to } \Delta\mathrm{VFF} = \frac{\Delta(n^2)_{\mathrm{exp}} - \Delta(n^2)_{\mathrm{norm}}}{\Delta(n^2)_{\mathrm{exp}}} \times 100 \tag{8}$$

or

$$\%\Delta(n^2) \text{ due to } \Delta\mathrm{VFF} = \left[1 - \frac{(n^2_{\mathrm{H,norm}} - n^2_{\mathrm{F,norm}})}{(n^2_{\mathrm{H,exp}} - n^2_{\mathrm{F,exp}})}\right] \times 100 \tag{9}$$

Density, refractive index, van der Waals volume, and fractional free volume are shown in Table 1. The

Table 1. Density, 3-D Average Refractive Index, van der Waals Volume (VDW), and Estimated Fractional Free Volume (VFF)

polymer	density (g/cm^3)	$n = (2n_{TE} + n_{TM})/3$	VDW$_{Bondi}$	VFF$_{exp}$
6FDA−PDA	1.4494 ± 0.0008	1.587717 ± 0.003666	223.17	0.3736 ± 0.000346
6FDA−TFPDA	1.5305	1.545833 ± 0.0008	237.09	0.3832
6FDA−DAT	1.4316 ± 0.005	1.580933 ± 0.0008	234.32	0.3675 ± 0.0022
6FDA−TFMPDA	1.4956 ± 0.00956	1.551333 ± 0.000666	241.98	0.3807 ± 0.000396
6FDA−2DAT	1.4250	1.561733 ± 0.0026166	245.47	0.3574
6FDA−2TFMPDA	1.5021 ± 0.0019	1.515233 ± 0.001966	260.79	0.3996 ± 0.00076

Table 2. Refractive Index Squared: Experimental and Normalized

polymer	n^2_{exp}	norm. to VFF	n^2_{norm}
6FDA−PDA	2.52084 ± 0.011657	0.3784	2.5034 ± 0.0127
6FDA−TFPDA	2.3896 ± 0.0024739	0.3784	2.4055 ± 0.00251
6FDA−DAT	2.4994 ± 0.0025301	0.3741	2.4762 ± 0.0102
6FDA−TFMPDA	2.4066 ± 0.0020689	0.3741	2.4288 ± 0.0156
6FDA−2DAT	2.4390 ± 0.0081799	0.3785	2.3704 ± 0.00766
6FDA−2TFMPDA	2.2959 ± 0.0059638	0.3785	2.3620 ± 0.00886

Table 3. Percent of Change in Dielectric Constant (n^2) due to Change in Fractional Free Volume[a]

polymer pair	%$\Delta\epsilon'_{exp}$ due to ΔVFF
(6FDA−PDA) → (6FDA−TFPDA)	25 ± 20
(6FDA−DAT) → (6FDA−TFMPDA)	49 ± 31
(6FDA−2DAT) → (6FDA−2TFMPDA)	94 ± 12

[a] Values for free volume contributions to change in dielectric constant (ϵ' or n^2) are the same as the free volume contributions to the change in the refractive index itself (n). There is not a square root relationship between these two sets of results.

Table 4. Percent of Change in Refractive Index (n) due to Change in Fractional Free Volume[a]

polymer pair	%Δn_{exp} due to ΔVFF
(6FDA−PDA) → (6FDA−TFPDA)	25 ± 20
(6FDA−DAT) → (6FDA−TFMPDA)	49 ± 31
(6FDA−2DAT) → (6FDA−2TFMPDA)	94 ± 12

[a] See footnote *a*, Table 3.

explicit TM and TE values of the refractive indexes can be found in ref 8. Table 2 shows the refractive index squared, the free volume value normalized to, and the resulting normalized value of ϵ' or n^2. The results of each pair comparison are shown in Table 3.

For a given polymer pair, the percentage of the experimental difference in dielectric constant that is due to differences in free volume is shown and is found to be very substantial.

The polymers 6FDA−PDA and 6FDA−TFPDA that were most similar in their fractional free volume had the smallest free volume contribution to the change in dielectric constant and refractive index. This may be because they both have planar diamine phenyl rings, and the difference in their ability to pack is relatively small. The polymers 6FDA−2DAT and 6FDA−2TFMPDA had the greatest apparent difference in their fractional free volumes and had the largest free volume contribution to the observed decrease in dielectric constant and refractive index. This may be because 6FDA−2DAT appears to pack efficiently (perhaps better than expected) while 6FDA−2TFMPDA packs quite loosely.

Refractive Index Results. While n^2 is used for the normalization procedure, as the CM/LL model requires, the magnitude of the role of free volume changes to the decrease in the refractive index (n) itself can easily be calculated as well. It is found that these results are quantitatively the same as those for the dielectric constant (n^2). This is shown in Table 4 for emphasis, though it differs from Table 3 only in the column heading. These results are obtained by taking the measured refractive index and the square root of the normalized refractive index squared for each material and performing a difference calculation.

$$\%\Delta(n) \text{ due to } \Delta\text{VFF} = \frac{\Delta(n)_{exp} - \Delta(n)_{norm}}{\Delta(n)_{exp}} \times 100 \quad (10)$$

or

$$\%\Delta(n) \text{ due to } \Delta\text{VFF} = \left[1 - \frac{(\sqrt{n^2_{H,norm}} - \sqrt{n^2_{F,norm}})}{(n_{H,exp} - n_{F,exp})}\right] \times 100 \quad (11)$$

Relevance to Low-Frequency Permittivity. Low-frequency dielectric constant values could not be used in this analysis because of the inherent difficulties in making highly accurate capacitance-based ϵ' measurements and because, at the lower frequencies, differences in dipole orientation polarization between polar fluorinated and nonpolar hydrogen analogs further complicated comparison. However, it can be said that at lower frequencies the free volume contribution to the observed change in relative permittivity upon fluorine substitution could be still greater than that reported here for optical frequencies. This would be most likely in cases where additional dipole orientation polarization resulting from asymmetric substitution of a fluorinated group contributes significantly to the measured relative permittivity of the fluorine-containing species.

Caveats and Future Work. In all cases, the error range obtained by propagating the highest and lowest possible values throughout the multiple steps of the calculation is large. Despite this, these results suggest a strong and, in some cases, dominant role of free volume changes in lowering the dielectric constant and refractive index with fluorine substitution.

For a given polymer, samples from different synthetic batches were used, the properties measured at different times after long durations and, in the case of density, by different techniques. Thus, variance in measured properties does not represent the tightest distribution experimentally possible. These calculations should be repeated using positron annihilation measurements of the fractional free volume, rather than relying solely on the estimated VFF values provided by the group additivity methods. However, this measurement technique has other drawbacks. While it is the technique of choice for direct measurements of free volume among samples of the same polymer, comparison between two different polymers may be less reliable. This is particularly true in cases where there is a significant difference in electronegativity, as this influences positron lifetime independently of free volume.[20] Substitution of fluorine for hydrogen may impart a great enough difference in electronegativity to render the positron lifetime technique less than ideal for the purposes of this work.

Conclusions

The percentage of the decrease in dielectric constant and refractive index observed upon fluorine substitution that is due to a simultaneous increase in fractional free volume has been estimated. Using a pair normalization method, the Clausius–Mossotti/Lorenz–Lorentz model, and a series of exact fluorine/hydrogen analogs, the free volume contribution has been found to range from 25% for the polyimides with the planar PDA and TFPDA diamine rings to 94% for the polyimides with the CH_3 and very bulky CF_3 groups.

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