Polarization Effects of Fluorine on the Relative Permittivity in Polyimides

G. Hougham,*,† G. Tesoro,‡ A. Viehbeck,† and J. D. Chapple-Sokol§

IBM T. J. Watson Research Center, Yorktown Heights, New York 10598,
Polytechnic University, 6 Metrotech Center, Brooklyn, New York 11201, and
IBM Microelectronics Division, Essex Junction, Vermont 05452

Received September 24, 1993; Revised Manuscript Received June 17, 1994®

ABSTRACT: The effect of fluorine incorporation on dielectric properties has been studied for a series of polyimides in order to distinguish between several contributing mechanisms to the generally observed decrease in the relative permittivity. Using low-frequency capacitance measurements after exhaustive in situ drying, in conjunction with refractive index measurements, the overall decrease in dielectric constant was semiquantitatively assigned between changes in the three modes of polarization via the use of fluorine/hydrogen and symmetric/unsymmetric analogs. These results suggest that replacement of hydrogen with fluorine always lowers the dielectric constant increment due to the electronic mode of polarization, has little effect on the atomic increment, and in the case of asymmetric fluorine substitution, results in an increase in the orientation increment. Values for each of these effects are reported.

Introduction

Polyimides exhibit exceptional thermal and mechanical properties, are easily processable as thin films from soluble precursors, and have desirable dielectric properties. The polyimides that are most widely used in the microelectronics industry have relative permittivity (dielectric constant or ϵ') values in the range 2.9–3.4. Since signal propagation speed and wiring density in multichip packaging are dependent on the dielectric constant, considerable effort has been expended in the last decade to design and synthesize new polyimides with lower dielectric constants. The greatest concentration of effort toward this end has involved the incorporation of fluorine atoms in the chemical structures.

The introduction of fluorine into polyimides can effect many properties, often in technologically desirable directions. These include thermal stability,[1,2] moisture absorption,[3-5] optical properties,[6-9] and dielectric constant—the property under consideration here.[2,3,10-14] While these fluorine-containing polyimides hold promise for use in microelectronic packaging due to improved signal transmission rates,[15] they have some limitations, in part because of the often greater solubility, lower glass transition temperatures (T_g), and higher coefficients of thermal expansion (CTE) compared to fluorine-free counterparts. However, highly fluorinated polyimides have recently been reported that do not share these typical drawbacks; for example refer to ref 16.

Dielectric Properties of Fluorinated Polyimides

While the simple and often correct assumption concerning the correlation of a lower dielectric constant with fluorine incorporation has been a valuable working hypothesis, it is now evident that further advancement of polymer properties could benefit from fundamental studies designed to dissect the bulk observed behavior between the myriad of contributing phenomena. Results of such studies may be useful in guiding future synthetic efforts.

Because fluorine substitution affects many, often interdependent, properties, the isolation of specific property dependencies on fluorine replacement is difficult. An important example of this is the effect of fluorine substitution on dielectric constant because the increased hydrophobicity caused by fluorination decreases the ambient dielectric constant by elimination of water from the polymer, while the incorporation of fluorine also affects the intrinsic properties of the polymer in several ways irrespective of the moisture effect. Most published dielectric data were measured under variable ambient relative humidity conditions; therefore the distinction between these effects has been lost.

Considerable progress in understanding molecular processes that lead to improved dielectric properties, in fluorine-containing polyimides, was made at NASA Langley. Dielectric properties of polyimides had been investigated with the objective of identifying specific physical and chemical factors that affect the dielectric constant.[12] The important role of chain-to-chain electronic interactions was considered, and in subsequent work these authors studied the effect of changes in free volume on the dielectric constant and found that increased free volume could be correlated with a decrease in dielectric constant.[17,18] Some previous work of our own has shown that, on average, the decrease in dielectric constant, which could be attributed solely to changes in free volume accompanying fluorine substitution, was often greater than 50% of the total decrease.[19] It has been noted elsewhere that the incorporation of fluorine into polyimides can increase the dipole moment and thus has the potential to increase dipole orientation polarization, but it was suggested that other effects overcame those increases, if indeed they were occurring.[2]

Since fluorine substitution can change the amount of free volume, the moisture absorption, and the polarizability in several ways, and each of these can independently affect the dielectric constant, we have tried to deconvolute the observed decreases in dielectric constant into their component contributing factors. This report addresses the effect of fluorine on the three modes of polarization: dipole orientation, atomic, and electronic. The effects of fluorine substitution on the dielectric constant due to concomitant changes in free volume and moisture absorption are considered elsewhere.[19-22]

---

† IBM T. J. Watson Research Center.
‡ Polytechnic University.
§ IBM Microelectronics Division.
® Abstract published in *Advance ACS Abstracts*, September 1, 1994.

0024-9297/94/2227-5964$04.50/0

Background

The relationship between the dielectric constant, density, and polarizability is often modeled using the Clausius–Mossotti relationship shown in eq 1. As the total polarizability (α) increases, the dielectric constant (ϵ') also increases. A brief description[23,24] of the origin of the three

$$\frac{\epsilon' - 1}{\epsilon' + 2}\frac{M_w}{\rho} = \frac{N_A\alpha}{3\epsilon'_o} \tag{1}$$

modes of polarization which contribute to the total polarization will allow a better understanding of their relationship with chemical substitutions and with the manner in which fluorine can affect each one.

Electronic polarization is the slight skewing of the equilibrium electron distribution relative to the positive nuclei to which it is associated. Since only the movement of electrons is involved, this process can occur very rapidly and typically has a time constant of around 10^{-15} s.

The atomic polarization results from rearrangement of nuclei in response to an electric field. The positive nuclei are attracted to the negative pole of the applied field. However, the movement of heavy nuclei is more difficult to initiate and reverse than that of electrons and so cannot follow an oscillating field at as high a frequency as the electron response.

Dipole orientation polarization results from the redistribution of charge when a group of atoms with a net permanent dipole moment reorients itself in space in response to an electric field. Since large group masses must reorient, this process is necessarily slower than either electronic or atomic polarization, and even in the gas phase will have time constants on the order of 10^{-9} s because of the larger inertia that must be overcome to reverse the direction of movement in each cycle of electric field oscillation. In the liquid or solid phases large intermolecular forces must be overcome, which slows the process further and decreases the polarization possible under all but static conditions. The dipole orientation polarization is often the dominant mode of polarization contributing to the dielectric constant in liquids and gases. In solids, dipole movement is usually restricted to the point where this becomes less significant than the electronic mode, but this is not always the case, as illustrated by polymers such as poly(vinyl fluoride) where enough dipole mobility exists to increase the dielectric constant dramatically ($\simeq 8$). These vinyl fluoride materials are near their glass transition temperatures at room temperature (where their dielectric constants were measured) and thus have substantial chain mobility. In polyimides, however, room temperature measurements are hundreds of degrees below the T_g, and molecular motion is severely limited.

There are some ways in which the three modes of polarization can interact, but in most cases, they act essentially separately and are therefore additive, as is shown in eq 2. If we substitute this into eq 1 we can see

$$\alpha_{tot} = \alpha_e + \alpha_a + \alpha_o \tag{2}$$

how each mode of polarization affects the dielectric constant.

$$\frac{\epsilon' - 1}{\epsilon' + 2}\frac{M_w}{\rho} = \frac{N_A(\alpha_e + \alpha_a + \alpha_o)}{3\epsilon'_o} \tag{3}$$

There are other models to describe these relationships, but regardless of the exact one used, the dielectric constant will always scale with the polarizability. The greater the sum of the three modes of polarization, the greater the dielectric constant will be. Because of the different time constants of the three modes of polarization, it follows that the dielectric constant will be frequency dependent.

At optical frequencies, where only electronic polarization is occurring, the dielectric constant can be found by the application of Maxwell's identity, shown in eq 4. The dielectric constant increment due to electronic polarization

$$\epsilon' = n^2 \tag{4}$$

only can be written as ϵ'_e, that for atomic polarization only as ϵ'_a, and that due to dipole orientation polarization as ϵ'_o. Since $n^2 = \epsilon'_e$ we can also denote ϵ'_e as ϵ'_{n^2}. Since the low-frequency (1 kHz, dry) value of the dielectric constant is composed of all three modes of polarization, it is denoted $\epsilon'_{o,a,e}$ and can also be referred to as $\epsilon'_{1\ \mathrm{kHz,\ dry}}$ (which in the context of this work will be designated simply as $\epsilon'_{1\ \mathrm{kHz}}$ since all of the polymers wer exhaustively dried before measurement) and is roughly equivalent to what is often referred to as the static dielectric constant, or ϵ'_s. This equivalency is far from perfect, however, since the materials under study are glassy solids and are unable to reach the maximum orientation polarization that the static term implies.

Following from the additivity of the different modes of polarization, the dielectric constant is assumed also to be essentially the sum of the dielectric constant increments due to each mode of polarization separately, as shown in eq 5. Our aim in this work was to determine the change

$$\epsilon'_{tot} \simeq \epsilon'_e + \epsilon'_a + \epsilon'_o \tag{5}$$

in each increment of the dielectric constant due to change in each of the three modes of polarization that occurs with fluorine substitution. The change in the electronic increment was straightforward to determine and predictably negative in direction. The change in the atomic mode was uncertain in both direction and magnitude. While α_a has anecdotally been considered small in magnitude, the change in ϵ'_a still had to be unambiguously determined to enable finding the change in the dipole orientation increment. The latter is accomplished by evaluation of the difference term $[\epsilon'_{o(\mathrm{asymm\ f\ subst})} - \epsilon'_{o(\mathrm{non\ f\ analog})}]$, which represents the change in the dipole orientation increment of the dielectric constant upon substituting a fluorine atom or CF_3 group for an H atom or a methyl group. A difficulty in finding the value of this difference term arises because we do not have discrete values of ϵ'_a for each material. If we did have values for the dielectric constant in each of the three critical frequency regimes, $\epsilon'_{o,a,e}$(1 kHz or pseudostatic), $\epsilon'_{e,a}$(n^2 infrared), and ϵ'_e(n^2 optical), we could obtain values for each dielectric constant increment by simple sequential subtraction of terms. It is often prohibitively difficult to accurately measure the dielectric constant in the far infrared on thin films, although considerable effort is being devoted to perfecting these techniques.[25–27]

Determining changes in orientation polarization upon substitution of a fluorinated group is, however, still possible because we are not concerned with the absolute values of ϵ'_e, ϵ'_a, or ϵ'_o, but only with the change in these quantities upon fluorine substitution for otherwise exactly analogous polymer structures.

We use an indirect method for estimating the magnitude of the change in the ϵ'_a associated with the replacement of hydrogen by fluorine, which then subsequently allows the estimation of the change in dielectric constant due to change in the orientational component, $\Delta\epsilon'_o$. This is done via measurements at only two extreme frequencies; the very low frequency of 1 kHz to give $\epsilon'_{o,a,e}$ and at the optical frequency 632.8 nm to give ϵ'_e.

This method will be described explicitly in the context of the first polymer system. Appropriate relations for other systems will be presented without derivation since they are obtained in analogous fashions.

Experimental Section

Dielectric constant measurements were carried out at 1 kHz using a Polymer Laboratories DETA system, consisting of a General Radio GR1689 capacitance bridge, a stainless steel parallel plate fixture in a furnace heated by a computer driven temperature controller. Fixtures were modified to accommodate 16 mm diameter samples. Samples were prepared by drying poly(amic acid) solutions onto a $^1/_8$ in. quartz disk in a carefully leveled vacuum oven, heating to 60 °C under 20 in. (Hg) vacuum with a slight nitrogen purge overnight. Samples were cured to 350 °C and cooled in a tube furnace under a steady stream of N_2 at all times. The film was released in a dilute (5%) HF solution (in fume hood) and was then water washed and dried. Films were clamped into a mask with opposing 16 mm openings on each side and were coated with between 400 and 500 Å gold under a 10^{-7} Torr vacuum on both sides. This thickness was found to have adequate conductivity to negate air-gap effects while being thin enough to allow facile z-direction diffusion of water out of the polymer bulk during drying. The average thickness of the polymer film within the sputtered electrode area was determined by making approximately 60 measurements on each sample, using an electronic micrometer with a 2 mm anvil. This high-resolution thickness survey proved essential to achieving the desired reproducibility in dielectric constant determinations. All films were in the 100–200 μm thickness range. The sample was introduced into the parallel plate fixture in the furnace and was heated at 0.5 °C/min under vacuum with a gentle N_2 purge to 200 °C. It was then cooled without reexposure to ambient atmosphere. The dry dielectric constant was then measured at room temperature and recorded.

The out-of-plane refractive indices (TM) were measured with a Metricon prism coupler using a HeNe laser.

Polymers were synthesized according to procedures described in detail elsewhere.[20,22] Structures are shown in Figure 1.

Results

Results of the dielectric constant measurements are shown in Table 1.

To independently determine the change in the dielectric constant due to the change in each mode of polarization ($\Delta\epsilon'_e$, $\Delta\epsilon'_a$, and $\Delta\epsilon'_o$) requires a set of hydrogen/fluorine and symmetric/asymmetric analogs. Depending on the exact type of substitution under study, sets of either three or four related polymers are required for the complete determination.

Three cases will be considered: replacement of hydrogen by fluorine, replacement of a methyl group by a trifluoromethyl group, and replacement of a hydrogen by a trifluoromethyl group on the amine phenyl ring.

Substitution of Fluorine for Hydrogen. The first case is the replacement of hydrogen by fluorine in the polymer pair 6FDA-PDA and 6FDA-FPDA. The symmetric fluorinated analog employed was 6FDA-TFPDA.

A rough indication of the behavior of this first system can be obtained by considering the following plots. Figure 2a shows the 1 kHz, dry and n^2 data for both 6FDA-PDA and 6FDA-TFPDA.

Because there should be no change in dipole moment with symmetric substitution, there should be no change in the dipole orientation polarization. Thus any change in the difference between the high- and the low-frequency values between the two materials could be assigned to changes in the atomic polarizability. As the $\Delta\epsilon'_{e,a,o}$ line appears to parallel the $\Delta\epsilon'_e$ line, there is apparently no significant change in ϵ'_a upon fluorination. We can then look at Figure 2b, which shows the data for the polymer pair 6FDA-PDA and the nonsymmetric 6FDA–FPDA. In this case the lines are not parallel, and the difference between the high- and low-frequency values increases when fluorine replaces hydrogen. Since we know from the symmetric case that $\Delta\epsilon'_a \simeq 0$, we can assign the deviation from parallelism to the change in the dielectric constant increment due to a change in dipole orientation polarization.

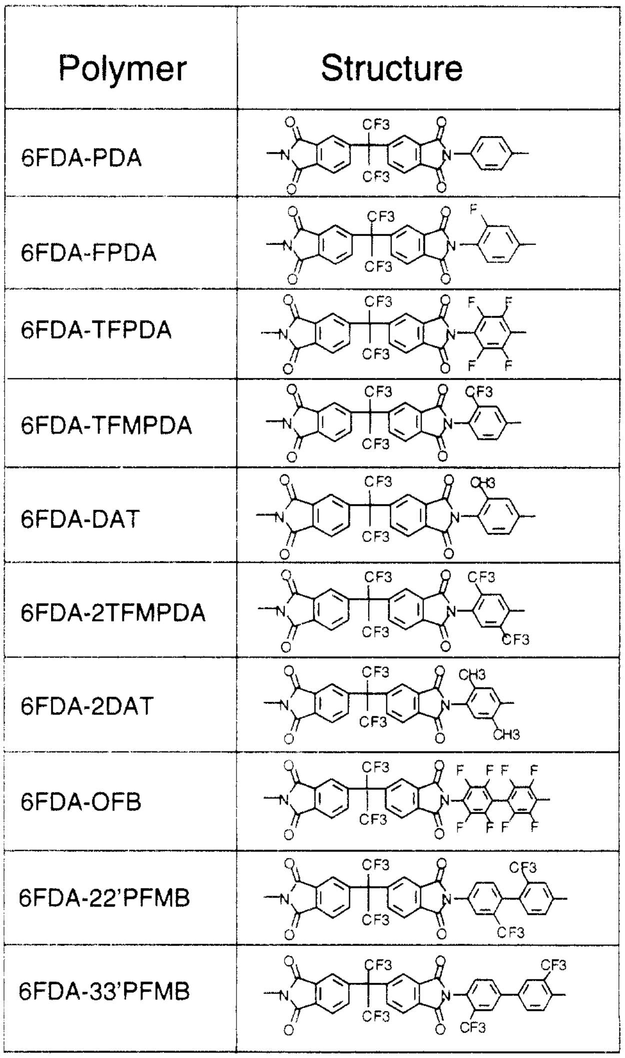

Figure 1. Abbreviations and structures of polyimide repeat units.

Table 1. Dielectric Data

polymer	$n^2_{632.8\ \mathrm{nm}}$	$\epsilon'_{1\ \mathrm{kHz,\ dry}}$
6FDA-PDA	2.506	2.81 ± 0.024
6FDA-FPDA	2.4825	2.85 ± 0.041
6FDA-DAT	2.4888 ± 0.0063	2.75 ± 0.023
6FDA-TFMPDA	2.3975 ± 0.00185	2.72 ± 0.005
6FDA-2DAT	2.42923 ± 0.0102	2.74 ± 0.039
6FDA-2TFMPDA	2.28872 ± 0.0058	2.59 ± 0.03
6FDA-TFPDA	2.3756 ± 0.0025	2.68 ± 0.046
6FDA-OFB	2.3492 ± 0.012	2.55 ± 0.02
6FDA-22'PFMB	2.3823 ± 0.0007	2.715 ± 0.035
6FDA-33'PFMB	2.328	2.582 ± 0.009

These observations can be put on a more quantitative footing with simple algebraic manipulation and the

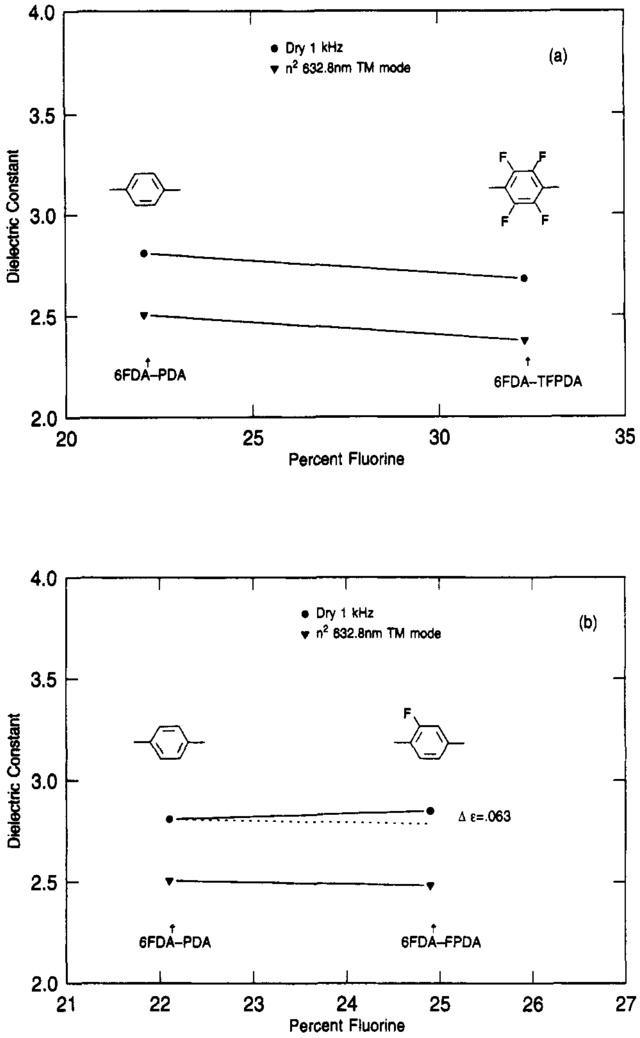

Figure 2. (a) Symmetric substitution. 6FDA-PDA and 6FDA-TFPDA. Lines between points highlight the parallel change in ϵ' and n^2 with substitution of four fluorine atoms on the ring. (b) Asymmetric substitution. 6FDA-PDA and 6FDA-FPDA. The dashed line parallel to the line connecting n^2 data points represents the expected position of ϵ' if no change in orientation or atomic polarization were occurring.

assumption of the validity of eq 5. The first polymer, 6FDA-PDA, which we will call material A, is unsubstituted on the amine ring. The second polymer, 6FDA-FPDA, which we will call material B, is singly substituted with a fluorine atom. In order to know whether the dipole associated with the fluorine group allows dipole orientation polarization to raise the dielectric constant above what it would be otherwise, data are required from a third material, 6FDA-TFPDA, which we will call C, which is symmetrically tetrasubstituted with the same substituent as material B. Overall, we would like to obtain values for the following three difference terms:

$$\Delta\epsilon'_e = [\epsilon'_e(B) - \epsilon'_e(A)] \qquad (6)$$

$$\Delta\epsilon'_a = [\epsilon'_a(B) - \epsilon'_a(A)] \qquad (7)$$

$$\Delta\epsilon'_o = [\epsilon'_o(B) - \epsilon'_o(A)] \qquad (8)$$

The first is a simple difference between the square of the refractive indices of the two species.

$$[\epsilon'_e(B) - \epsilon'_e(A)] = [n^2(B) - n^2(A)] \qquad (9)$$

Inserting the appropriate values gives

$$[\epsilon'_e(B) - \epsilon'_e(A)] = -0.0235 \qquad (10)$$

Thus the substitution of a single hydrogen atom with fluorine results in a decrease of 0.0235 in the optical frequency dielectric constant. To find the change in the atomic term $[\epsilon'_a(B) - \epsilon'_a(A)]$, we begin by solving eq 11 for the atomic difference term between polymers C and A. Assuming the validity of eq 5 allows the mixed terms to be separated. The fact that C is a symmetric analog of B

$$[\epsilon'_{o,a}(C) - \epsilon'_{o,a}(A)] = [\epsilon'_o(C) - \epsilon'_o(A)] + [\epsilon'_a(C) - \epsilon'_a(A)] \qquad (11)$$

is important. Since there is no change in dipole moment between the unsubstituted A and the symmetric tetrasubstituted C, we can set the orientation difference term to zero. After rearrangement this becomes

$$[\epsilon'_a(C) - \epsilon'_a(A)] = [\epsilon'_{o,a}(C) - \epsilon'_{o,a}(A)] - 0 \qquad (12)$$

The mixed atomic/orientation terms can be evaluated by subtracting the optical from the low-frequency dielectric constants for each material, as shown below.

$$\epsilon'_{o,a}(A) = [\epsilon'_{o,a,e}(A) - \epsilon'_e(A)] \qquad (13)$$

$$\epsilon'_{o,a}(C) = [\epsilon'_{o,a,e}(C) - \epsilon'_e(C)] \qquad (14)$$

Substituting these cross terms into eq 12 allows the determination of the change in the dielectric constant due to changes in the atomic polarization that accompanies four replacements of fluorine for hydrogen. This gives

$$[\epsilon'_a(C) - \epsilon'_a(A)] = [\epsilon'_{o,a,e}(C) - \epsilon'_e(C)] - [\epsilon'_{o,a,e}(A) - \epsilon'_e(A)] \qquad (15)$$

It is then assumed that the change that would accompany fewer replacements of the identical type would be proportional to the number of such replacements, since atomic polarization is essentially a bond-localized phenomenon. So, it is taken to be one-fourth of this value for the 6FDA-PDA to 6FDA-FPDA pair, as shown below.

$$[\epsilon'_a(B) - \epsilon'_a(A)] = \frac{[\epsilon'_a(C) - \epsilon'_a(A)]}{4} \qquad (16)$$

We can put these all togther in one relation, and then the same relation can be expressed entirely in terms of measurable quantities for clarity.

$$[\epsilon'_a(B) - \epsilon'_a(A)] = \frac{[\epsilon'_{o,a,e}(C) - \epsilon'_e(C)] - [\epsilon'_{o,a,e}(A) - \epsilon'_e(A)]}{4} \qquad (17)$$

$$[\epsilon'_a(B) - \epsilon'_a(A)] = \frac{[\epsilon'_{1\,\mathrm{kHz}}(C) - \epsilon'_{n^2}(C)] - [\epsilon'_{1\,\mathrm{kHz}}(A) - \epsilon'_{n^2}(A)]}{4} \qquad (18)$$

If we plug in the appropriate measured values, we get

$$[\epsilon'_a(B) - \epsilon'_a(A)] = 0.0001 \pm 0.018 \qquad (19)$$

Despite the large error range, this suggests that the replacement of hydrogen with fluorine on a phenyl ring has little effect on the dielectric constant increment due to atomic polarization. To find the third or the orientation

Table 2. Change in Dielectric Constant Increments

polymer pair[a]	$\Delta\epsilon'_e$[b]	$\Delta\epsilon'_a$	$\Delta\epsilon'_o$
PDA → FPDA	−0.0235	+0.0001 ± 0.01813	+0.0632 ± 0.0806
PDA → TFPDA	−0.1304 ± 0.0025	+0.0004 ± 0.0725	assumed = 0 by symmetry
DAT → TFMPDA	−0.0913 ± 0.00815	−0.00475 ± 0.0425	+0.06605 ± 0.0787
2DAT → 2TFMPDA	−0.1405 ± 0.0044	−0.00949 ± 0.085	assumed = 0 by symmetry
PDA → TFMPDA	−0.1085 ± 0.00185	−0.00136	+0.01971 ± 0.0299
PDA → 2TFMPDA	−0.2173 ± 0.0058	−0.00272 ± 0.05982	assumed = 0 by symmetry
22′PFMB → OFB	−0.0331 ± 0.0127	assumed = 0	+0.1319 ± 0.0677
33′PFMB → OFB	+0.0211 ± 0.012	assumed = 0	+0.0533 ± 0.042

[a] All materials based on 6FDA dianhydride. [b] Reported value includes some change in $\Delta\epsilon'_e$ due to changes in fractional free volume (ΔV_{ff}), on average about half. For a better approximation of the fraction due to ΔV_{ff} see refs 19 and 21. Values for $\Delta\epsilon'_a$ and $\Delta\epsilon'_o$ are due only to changes in polarization, and no contribution from ΔV_{ff} is included.

difference term (eq 8), we can begin by rearranging the following equation.

$$[\epsilon'_{o,a}(B) - \epsilon'_{o,a}(A)] = [\epsilon'_o(B) - \epsilon'_o(A)] + [\epsilon'_a(B) - \epsilon'_a(A)] \tag{20}$$

This rearranges to

$$[\epsilon'_o(B) - \epsilon'_o(A)] = [\epsilon'_{o,a}(B) - \epsilon'_{o,a}(A)] - [\epsilon'_a(B) - \epsilon'_a(A)] \tag{21}$$

The last bracketed difference term in the equation is just the atomic difference term of eq 18. So what remains is to fill in the middle combination term. The expression for polymer A was found in eq 13 already and that for polymer B is of the identical form. If we make the appropriate substitutions, we get

$$[\epsilon'_o(B) - \epsilon'_o(A)] = [\epsilon'_{o,a,e}(B) - \epsilon'_e(B)] - [\epsilon'_{o,a,e}(A) - \epsilon'_e(A)] - \left[\frac{[\epsilon'_{o,a,e}(C) - \epsilon'_e(C)]}{4} - \frac{[\epsilon'_{o,a,e}(A) - \epsilon'_e(A)]}{4}\right] \tag{22}$$

Or, to express this in terms of physical measurements only

$$[\epsilon'_o(B) - \epsilon'_o(A)] = [\epsilon'_{1\,\mathrm{kHz}}(B) - \epsilon'_{n^2}(B)] - [\epsilon'_{1\,\mathrm{kHz}}(A) - \epsilon'_{n^2}(A)] - \left[\frac{[\epsilon'_{1\,\mathrm{kHz}}(C) - \epsilon'_{n^2}(C)]}{4} - \frac{[\epsilon'_{1\,\mathrm{kHz}}(A) - \epsilon'_{n^2}(A)]}{4}\right] \tag{23}$$

Then, if we substitute the measured values, we get

$$[\epsilon'_o(B) - \epsilon'_o(A)] = 0.063 \mp 0.081 \tag{24}$$

This shows that the substitution of a hydrogen atom with a nonsymmetric fluorine atom on a phenyl ring results in a substantial increase in the dielectric constant increment due to orientation polarization—about 0.06. This value is moderate in terms of the actual impact on the dielectric properties in this case. Nevertheless, if this value of 0.06 is even close to accurate, it has important implications for the design of future high-performance materials. Asymmetric placement of fluorine atoms in any significant weight percent would have to be avoided if good dielectric properties were to be retained. If one such substitution increases the ϵ' by 0.06 over what it would be otherwise, then multiple asymmetric substitution in the same repeat unit could lead to substantial increases, defeating the original intent of the incorporation of fluorine in the macromolecule.

The changes to the three dielectric constant increments are summarized in Table 2.

The addition of fluorine decreases the electronic component of polarization regardless of symmetry of placement, so the observed change in the overall bulk dielectric constant upon fluorination is always the sum of a decreased ϵ'_e and either an increased ϵ'_o with asymmetrical placement or an unchanged ϵ'_o with symmetrical placement of the fluorine atoms. In addition, there is virtually no apparent difference in ϵ'_a to consider. Thus the observed overall change in the bulk ϵ' with fluorination can be a net decrease if there is no additional orientation polarization or if the additional orientation polarization is outweighed by the decrease in the electronic polarization. It could be a net increase if the additional orientation polarization outweighed the change to the electronic polarization, or there could be no net change at all if the increased orientation polarization were to balance the decreased electronic polarization.

The magnitude of the error cannot be ignored. The size of the error bar forces us to consider these average values as suggestive of the effects discussed, but we cannot say with certainty that they have the magnitudes given. As we will show in the remaining cases, in every instance of nonsymmetric fluorine placement the $\Delta\epsilon'_o$ is positive, thus considerably reducing the possibility that these positive $\Delta\epsilon'_o$ findings are coincidental.

Substitution of a Trifluoromethyl for a Methyl Group. To consider the effect of substitution of a trifluoromethyl group in place of a methyl group, we needed a set of four polymers, 6FDA-DAT (A), 6FDA-TFMPDA (B), 6FDA-2TFMPDA (C), adn 6FDA-2DAT (D). This gives us the H/F and symmetric/nonsymmetric analogs required for the initial determination of $\Delta\epsilon'_a$ and the subsequent determination of $\Delta\epsilon'_o$. The method is entirely analogous to that used in the previous example.

Again, first, to get a qualitative view, Figure 3a shows that upon going from dimethyl to a bis(trifluoromethyl) analog, there is no change in the dielectric constant increment due to atomic polarization, as evidenced by the apparently parallel lines. Figure 3b shows that upon substituting a single trifluoromethyl group for a methyl group there is a little net change in the low-frequency dielectric constant, $\epsilon'_{o,a,e}$, but the dielectric constant due to electronic processes only, ϵ'_e, drops considerably. Since we know that there is no significant change in the atomic polarizability with fluorine incorporation, as shown by the symmetric pair, then the low-frequency data should have decreased by the same amount as the n^2 data if it were not for a change in the orientation polarization. The fact that it did not is an indication that the increase in ϵ' due to orientation polarizability more or less balanced the decrease in ϵ' due to the decreases in the electronic polarizability. The difference between the observed low-frequency value and the value that it would have if there were no change in ϵ'_o (shown by the dotted line) is the magnitude of the change in the dielectric constant due to the dipole orientation process.

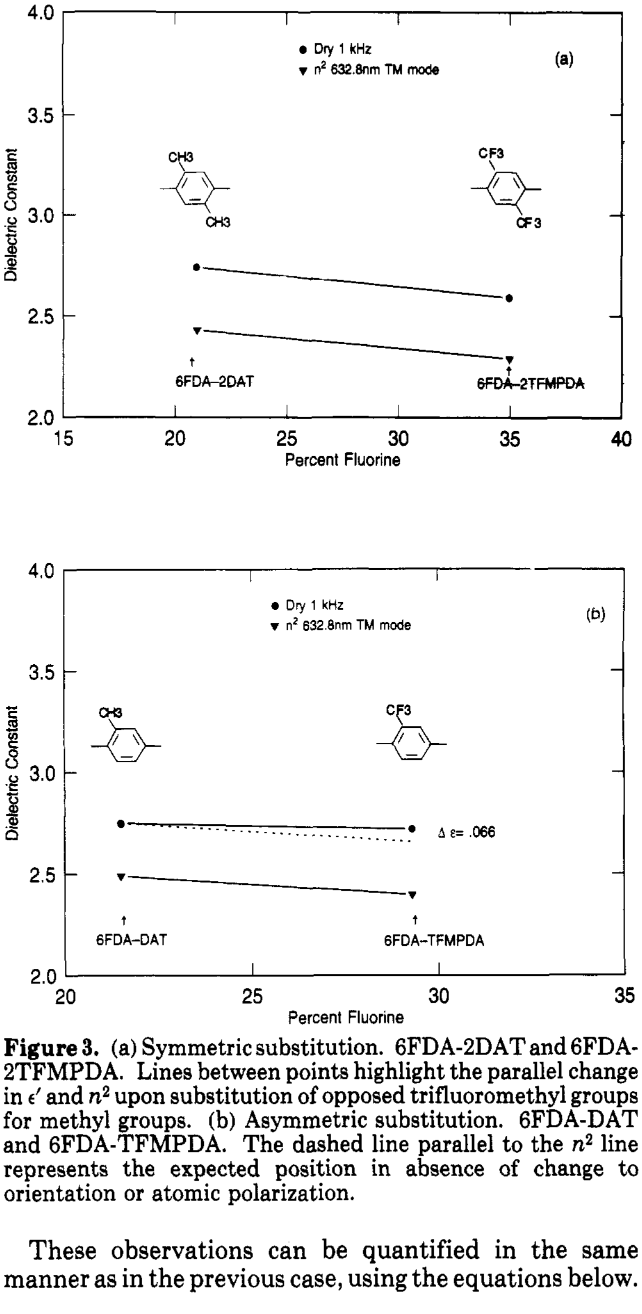

Figure 3. (a) Symmetric substitution. 6FDA-2DAT and 6FDA-2TFMPDA. Lines between points highlight the parallel change in ϵ' and n^2 upon substitution of opposed trifluoromethyl groups for methyl groups. (b) Asymmetric substitution. 6FDA-DAT and 6FDA-TFMPDA. The dashed line parallel to the n^2 line represents the expected position in absence of change to orientation or atomic polarization.

These observations can be quantified in the same manner as in the previous case, using the equations below.

$$[\epsilon'_{\mathrm{a}}(\mathrm{B}) - \epsilon'_{\mathrm{a}}(\mathrm{A})] = \frac{\epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{C})}{2} - \frac{\epsilon'_{n^2}(\mathrm{C})}{2} - \frac{\epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{D})}{2} + \frac{\epsilon'_{n^2}(\mathrm{D})}{2} \tag{25}$$

$$[\epsilon'_{\mathrm{o}}(\mathrm{B}) - \epsilon'_{\mathrm{o}}(\mathrm{A})] = \epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{B}) - \epsilon'_{n^2}(\mathrm{B}) - \epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{A}) + \epsilon'_{n^2}(\mathrm{A}) - \frac{\epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{C})}{2} + \frac{\epsilon'_{n^2}(\mathrm{C})}{2} + \frac{\epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{D})}{2} - \frac{\epsilon'_{n^2}(\mathrm{D})}{2} \tag{26}$$

The results for substitution of a single methyl group by a single trifluoromethyl group are shown in Table 2, and the apparent magnitude of the orientational effect is substantial.

Substitution of Trifluoromethyl for Hydrogen. The replacement of a hydrogen atom with a trifluoromethyl group is a more complex structural change than in the previous cases. While this is not the exact replacement of H for F atom types, it is nevertheless a case of considerable interest because it is a substitution option that frequently arises in practice. The set of materials for this comparison consists of 6FDA-PDA (A), 6FDA-TFMPDA (B), and 6FDA-2TFMPDA (C). The relations of interest are shown below.

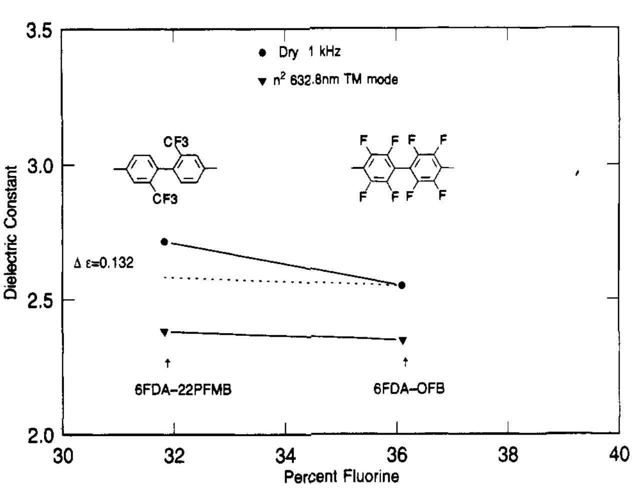

Figure 4. Plot showing a much higher change in ϵ' for 6FDA-22′PFMB, relative to 6FDA-OFB, than would be expected on the basis of only slightly lower fluorine content, which is shown as the dashed line. The difference is due to increased orientational polarization from asymmetric substitution of polar CF_3 groups.

$$[\epsilon'_{\mathrm{a}}(\mathrm{B}) - \epsilon'_{\mathrm{a}}(\mathrm{A})] = \frac{\epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{C})}{2} - \frac{\epsilon'_{n^2}(\mathrm{C})}{2} - \frac{\epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{A})}{2} + \frac{\epsilon'_{n^2}(\mathrm{A})}{2} \tag{27}$$

$$[\epsilon'_{\mathrm{o}}(\mathrm{B}) - \epsilon'_{\mathrm{o}}(\mathrm{A})] = \epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{B}) - \epsilon'_{n^2}(\mathrm{B}) - \epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{A}) + \epsilon'_{n^2}(\mathrm{A}) - \frac{\epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{C})}{2} + \frac{\epsilon'_{n^2}(\mathrm{C})}{2} + \frac{\epsilon'_{1\ \mathrm{kHz,\ dry}}(\mathrm{A})}{2} - \frac{\epsilon'_{n^2}(\mathrm{A})}{2} \tag{28}$$

The results for this comparison are shown in Table 2.

As in the other cases, there is a significant drop in ϵ' due to a decrease in the electronic polarization, little change in atomic polarization, and surprisingly, a smaller apparent increase in the dipole orientation polarization than in the other asymmetric cases.

Replacement of CF_3 for H (Equivalent). Lastly, we would also like to consider two related cases, which again are not comparisons of exact H/F analogs, but which are very instructive concerning the magnitude of dipole orientation contributions to the dielectric constant from asymmetric CF_3 substitution. These are the change in ϵ'_{o} between the symmetric 6FDA-OFB and the nonsymmetric 6FDA-22′PFMB and separately with 6FDA-33′PFMB. We will consider these pairs in turn. From the standpoint of determining the change in the dielectric constant from dipole orientation of the CF_3-substituted phenyl rings, this comparison is the rough equivalent of comparing 6FDA-benzidine to 6FDA-22′PFMB. Since the benzidine polymer was not available, the closest structure that had no dipole moment associated with the phenyl rings of the amine was used—6FDA-OFB. While 6FDA-OFB and 6FDA-22′PFMB differ in the nature of their fluorine substitution, we have seen from the earlier comparisons that there is no change to the atomic mode upon change from H to F, CH_3 to CF_3, and H to CF_3, and so it seems reasonable to assume that there will be no signifcant change to the atomic mode between these structures when replacing both CF_3 for F and H for F. Figure 4 shows that while there is a small decrease in the dielectric constant due to electronic processes upon going from 6FDA-22′PFMB to 6FDA-OFB, as might be expected on the basis of a small change in percent fluorine, there is a disproportionately large decrease in the low-frequency

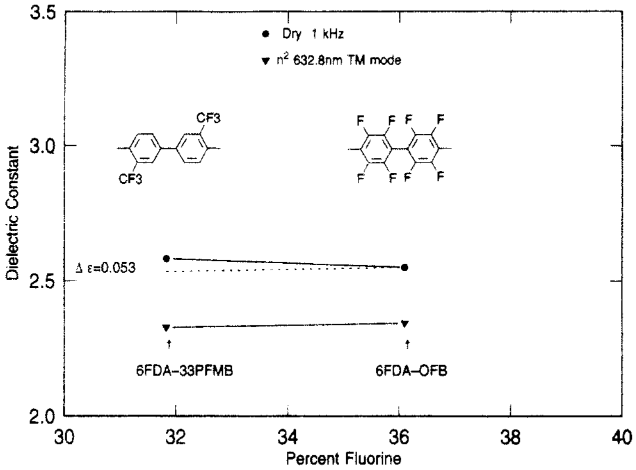

Figure 5. Plot showing a somewhat greater change in ϵ' with frequency, for 6FDA-33′PFMB relative to 6FDA-OFB. The difference between the 1 kHz solid line and the dashed line is due to orientation polarization from asymmetric substitution of polar CF_3 groups.

values. The consequent change in the difference between the high- and low-frequency values for the two materials can be associated with a larger dipole orientation contribution from asymmetrical 6FDA-22′PFMB.

Since $\Delta\epsilon'_a$ is assumed to be equal to zero in the PFMB cases, the $\Delta\epsilon'_o$ is obtained simply using the following, which is just the change in the difference between the low- and high-frequency values of the dielectric constant between the two materials.

$$\Delta\epsilon'_o = [\epsilon'_{1\,\mathrm{kHz}}(\mathrm{22PFMB}) - \epsilon'_{n2}(\mathrm{22PFMB})] - [\epsilon'_{1\,\mathrm{kHz}}(\mathrm{OFB}) - \epsilon'_{n2}(\mathrm{OFB})] \quad (29)$$

The results are shown in Table 2. The difference is about 0.13 or about 0.065 per freely rotating CF_3-substituted phenyl ring. The magnitude is similar to that of the CH_3/CF_3 case but greater than that of the previous H to CF_3 case to which it is most closely related.

The second of the two biphenyl cases is the comparison of 6FDA-OFB to 6FDA-33′PFMB. As can be seen in Figure 5 and Table 2, the $\Delta\epsilon'_o$ is smaller in this case, with a total value of around 0.04, or 0.02 per freely rotating group. Either this difference between the $\Delta\epsilon'_o$ for the two PFMB isomers is due to statistical variation, which is plausible given the size of the error bars, or it may be an indication that the 6FDA-33′PFMB case is more sterically hindered due to interaction of the CF_3 groups with the imide carbonyl groups. This interaction would limit rotation of the substituted phenyl ring to a smaller angle for a given applied torque and would result in a smaller polarization.

Discussion

The magnitude of the dipole orientation increment to the dielectric constant in all of the cases discussed is significant relative to the decrease in the electronic increment. This magnitude is often large enough to counter the decrease in dielectric constant due to decreases in electronic polarization in cases of CF_3 substitution, leading to little overall change in the bulk dielectric constant. It is large enough to more than compensate for decreases in the electronic polarization in cases of fluorine atom substitution, leading to actual increases in the bulk dielectric constant. Given these results, future efforts to synthesize high-performance polymers for low dielectric applications should maximize the symmetric substitution of all polar fluorine-containing groups.

The magnitude of the dipole orientation contribution is particularly surprising given that these measurements were made at temperatures nearly 300 deg below the glass transition and 150 deg. below the maxima of the β transition. β relaxations are very broad viscoelastic transitions involving molecular motions most likely associated with rotation of the phenyl ring in the diamino portion of the polyimide.[28-30] At temperatures entirely below the β relaxation envelope, significant rotation is precluded, and little orientation polarization should be possible. Room temperature dielectric measurements of these materials appear to be within the persistent low-temperature tail of the relaxation.[31] Certainly the dielectric constant at higher temperatures would be larger, due to still greater molecular mobility of the polar groups. Since typical use temperatures in thin film packaging are 60–80 °C, the material will be deeper into the β relaxation than at room temperature, and the effect of nonsymmetric fluorine on the relative permittivity could be still greater than reported here.

Conclusions

The changes in the dielectric constant resulting from changes in each of the three modes of polarization have been evaluated for a number of polyimide systems. It is evident that the change in the dielectric constant due to changes in the electronic mode of polarization always decreases with fluorine or trifluoromethyl substitution, that changes in the dielectric constant due to changes in the atomic mode are negligible, and that the change in the dielectric constant due to changes in dipole orientation polarization in the case of nonsymmetric substitution is always positive and has an average magnitude on the order of 0.05 per substituted ring.

These results can be implemented to practical advantage in optimizing dielectric properties by maximizing the number of symmetric fluorine or trifluoromethyl substituents on individual rings and avoiding nonsymmetric substitution patterns whenever possible.

Acknowledgment. The authors would like to thank S. Petrucci for valuable discussions.

References and Notes

(1) Harris, F. W.; Hsu, S. L. C. *High Perform. Polym.* **1989**, *1* (1), 3-16.
(2) Ichino, T.; Sasaki, S.; Matsuura, T.; Nishi, S. *J. Polym. Sci. Part A* **1990**, *28*, 323-331.
(3) Beuhler, A. J.; Burgess, M. J.; Fjare, D. E.; Gaudette, J. M.; Roginski, R. T. *Mater. Res. Soc. Symp. Proc.* **1989**, *154*, 73-90.
(4) Mercer, F. W.; McKenzie, M. T. *High Perform. Polym.* **1993**, *5*, 97-106.
(5) Goff, D. L.; Yuan, E. L.; Long, H.; Neuhaus, H. J. *Organic Dielectric* Materials with Reduced Moisture Absorption and Improved Electrical Properties. In *Polymeric Materials for Electronics Packaging and Interconnection*; Lupinski, J. H., Moore, R. S., Eds.; American Chemical Society: Washington, DC, 1989; pp 93-100.
(6) Reuter, R.; Franke, H.; Feger, C. *Appl. Opt.* **1988**, *27*, (21-1), 4565-4571.
(7) Omote, T.; Koseki, K.; Yamaoka, T. *Polym. Eng. Sci.* **1989**, *29*, (14), 945-949.
(8) St. Clair, A. K.; Stoakley, D. M.; St. Clair, T. L. *Pac. Polym. Prepr.* **1989**, *1*, 91-92.
(9) Husk, G. R.; Cassidy, P. E.; Gebert, K. L. *Macromolecules* **1988**, *21*, 1234-1238.
(10) Matsuura, T.; Nishi, S.; Ishizawa, M.; Yamada, Y.; Hasuda, Y. *Pac. Polym. Prepr.* **1989**, *1*, 87-88.
(11) Gerber, M. K.; St. Clair, T. L.; Pratt, J. R.; St. Clair, A. K. *NASA Tech. Mem.* 14206-1, 1-10.

(12) St. Clair, A. K.; St. Clair, T. L.; Winfree, W. P. *PMSE* **1988**, *59*, 28–32.

(13) St. Clair, A. K.; St. Clair, T. L.; Slemp, W. S. Optically Transparent/Colorless Polyimides. In *Proceedings of the 2nd International Conference on Polyimides. Recent Advances in Polyimide Science and Technology*; Weber, W. D., Gupta, M. R., Eds.; Society of Plastics Engineers: 1987; pp 16–36.

(14) Stoakley, D. M.; St. Clair, A. K. *NASA Tech. Memo.* 33–36 (Langley).

(15) Numata, S. Required Changes in Polyimides for Microelectronics. In *Polymers for Microelectronics-Science and Technology*; Tabata, Y., Mita, S., Nonogaki, S., Horie, K., Tagawa, S., Eds.; VCH: New York, 1990; pp 689–697.

(16) Feiring, A. E.; Auman, B. C.; Wonchoba, E. R. *Macromolecules* **1993**, *26* (11), 2779–2784.

(17) Singh, J. J.; St. Clair, T. L.; Holt, W. H.; Mock, W., Jr. *NASA Tech. Memo.* **1985**, 86431, 1–7.

(18) Singh, J. J.; Eftekhari, A.; St. Clair, T. L. *NASA Tech. Memo.* **1990**, 102625, 1–16.

(19) Hougham, G.; Viehbeck, A.; Tesoro, G.; Shaw, J. *Tech. Pap.—Soc. Plast. Eng.* **1990**, *90*, 445.

(20) Hougham, G.; Tesoro, G.; Viehbeck, A.; Chapple-Sokol, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (1).

(21) Hougham, G.; Tesoro, G.; Viehbeck, A.; Shaw, J. Submitted for publication.

(22) Hougham, G.; Tesoro, G.; Shaw, J. *Macromolecules* **1994**, *27*, 3642–3649.

(23) Blythe, A. R. in *Electrical Properties of Polymers*; Cambridge University Press: Cambridge, U.K. 1979; Chapter 2.

(24) Ku, C. C.; Liepins, R. *Electrical Properties of Polymers. Chemical Principles*; Hanser: Munich, Vienna, New York, 1987; Chapter 2.

(25) Firman, P.; Marchetti, A.; Xu, M.; Eyring, E. M.; Petrucci, S. *J. Phys. Chem.* **1991**, *95*, 55–61.

(26) Simonis, G. J. In *Handbook of Optical Constants of Solids*; Palik, E. D., Ed.; Academic Press: Orlando, FL, 1985; Chapter 8.

(27) Robertson, W. M.; Arjavalingam, G.; Hougham, G.; Kopcsay, G. V.; Edelstein, D.; Ree, M. H.; Chapple-Sokol, J. D. *Elec. Lett.* **1992**, *28* (1), 62–63.

(28) Hougham, G.; Tesoro, G.; Shaw, J. *PMSE* **1989**, *61*, 369.

(29) Arnold, F. E.; Shen, D.; Lee, C. J.; Harris, F. W.; Cheng, S. Z. D.; Starkweather, H. W. *J. Mater. Chem.* **1993**, *3* (2), 183–190.

(30) Cheng, S. Z. D.; Arnold, F. E.; Bruno, K. R.; Shen, D.; Eashoo, M.; Lee, C. J.; Harris, F. W. *Polym. Eng. Sci.* **1993**, *33* (21), 1373–1380.

(31) Hougham, G.; Jackman, T. To be published.