Opto-thermal characteristics of amorphous polyimides for optical applications

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Abstract: Polymeric components are desirable in optical and photonic applications because of their light weight, high impact resistance, and/or ability to be formed into sophisticated shapes or gradient index (GRIN) optics. However, relatively large thermal effects in polymers can limit applications. We studied a selected series of amorphous polyimides in order to evaluate their potential application in components of optical devices. Several of these polyimides have thermo-optic coefficients ($dn/dT$) and volume coefficients of thermal expansion (VCTE) about 50% smaller than those of standard optical polymers, such as PMMA and polycarbonate. Surprisingly, these low $dn/dT$ and VCTE values were found in amorphous polyimides which have sterically hindered, kinked linkages between phenyl rings. This suggests a different structural dependence than that found in previous studies, which showed that low thermal expansion in crystalline polyimides is correlated with a rigid linear backbone molecular structure. Thus, amorphous polyimides with favorable backbone structures represent a class of materials with improved thermo-optical stability for polymeric optical devices.

OCIS codes: (160.5470) Polymers; (120.4530) Optical constants; (120.6810) Thermal effects.

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1. Introduction

Polymers are of special interest in optical and photonic applications because of the significant advantages they offer. They can be lightweight and resilient, have high optical transparency, and are easily formed into sophisticated shapes. Numerous polymeric optical devices have been demonstrated to date, such as in the areas of optical communication, data transmission, storage, and display. In addition, multilayer polymer film techniques have enabled the fabrication of polymeric gradient index (GRIN) lenses that can reduce the size, mass and complexity of optical systems [1].

An important consideration in such applications is the thermal stability of the optical response [2]. Generally, an optical component is deemed thermally stable when both the physical dimensions and the refractive index are insensitive to temperature changes. This is an important consideration in optical applications because even small, thermally-induced changes in material properties can give rise to significant deterioration in device performance. In general, however, optical polymers exhibit relatively large thermal expansion and thermo-optic coefficients (CTE and $dn/dT$, respectively). Thus, suppressing thermal effects in optical polymers has been the subject of considerable research. Polyimides are a promising class of polymers that can exhibit both low CTE and high transparency. Transparent, processable polyimides are now available with in-plane linear CTE’s (LCTE’s) that match the low values found in common inorganic optical materials [3–5], thereby enabling the fabrication of reliable hybrid (organic/inorganic) devices. However, many of the polyimides with low in-plane LCTE’s still have relatively large out-of-plane LCTE’s, and hence large volume CTE’s (VCTE’s). The large VCTE’s generally correspond to large $dn/dT$’s in these materials. Furthermore, the anisotropic thermal expansion can also be associated with a temperature-dependent optical birefringence [6]. All of these properties can be problematic in optical device applications.

The objective of this work is to survey a set of polyimide molecular structures deemed likely to be good candidates for optical device applications. Several recent studies have addressed the connection between a polymer’s structure and its LCTE and VCTE. In one report [7], it was found that while the backbone structure influenced the VCTE of the polyimides being investigated, the LCTE anisotropy varied substantially with the synthesis
and/or processing conditions. Conversely, for each polyimide studied there, the VCTE was essentially independent of synthesis and processing. For most optical applications, where anisotropic thermal expansion can be problematic, this suggests the need to choose not only a backbone chemistry that minimizes VCTE but also the synthesis and processing methods that lead to an amorphous material, hence minimizing the anisotropy.

Another recent study [8] investigated aromatic polyimides by X-ray diffraction, and proposed interesting and useful structure-property relationships between the backbone chemistry and the corresponding LCTE and VCTE. While that study was done (by necessity) on crystalline polyimides, amorphous polymers such as those examined in the present work, which are intrinsically more isotropic in all relevant properties, are more likely to be appropriate in most optical applications.

In the current study, we investigate the influence of backbone chemistry on the thermal properties of a family of amorphous, optically transparent polyimides. Our amorphous polyimides were synthesized by reacting a dianhydride with a diamine to form a poly(amic) acid, which was subsequently thermally converted to the polyimide of interest. For the purpose of organizing our findings, we arrange our results on these polyimides in a matrix format, where the dianhydrides are the columns and the diamines are the rows. We combined four diamines with four dianhydrides using similar processing conditions. The component diamines and dianhydrides were chosen from polyimides that were previously reported to have reduced CTE and/or $dn/dT$, as well as reasonable optical transparency. Some of these were chosen to have flexible or bent linkages between phenyl rings, which increase the likelihood of forming amorphous polymers. Using relatively thick film samples of these polyimides, we measured the $dn/dT$ of each material and used the Lorentz-Lorenz model to obtain the corresponding VCTE. Furthermore, these results enabled a prediction of the fractional change in focal length with temperature for a notional simple lens made of each polyimide, which we used as a benchmark for comparing the suitability of these polyimides for eventually fabricating thermally stable polymeric optics. Note that within the context of this work, we use “thermal stability” to refer only to changes in the refractive index and physical dimensions as a function of temperature, rather than to changes in other physical properties of these materials.

2. Materials synthesis and sample preparation

Polyimides with good transmission in the visible and near-IR, as well as good processability, are a promising class of component materials for thermally stable polymeric optics. Progress in developing new, processable, transparent polyimides has been described recently [4,9]. The synthesis of solution-processable polyimides with low LCTE and improved transmission in the visible spectrum has also been described recently [5].

We prepared poly(amic acid) (PAA) solutions, the precursors of the polyimides we studied here, by polycondensation of tetracarboxylic dianhydrides and diamines in anhydrous $N,N'$-dimethylacetamide (DMAc, 99.8% purity, Alfa-Aesar) at room temperature. A typical procedure was as follows: diamine (5 mmol) was placed in a 50 mL round-bottom flask. The round-bottom flask, capped with a rubber septum, was then evacuated and backfilled with nitrogen gas (3 times). Anhydrous DMAc was added via syringe through the septum. Tetracarboxylic dianhydride (5 mmol) was then added as a powder to the diamine solution, with continuous magnetic stirring. At this point, the reaction mixture had an initial total solid content of ~30 wt%. The reaction mixture was stirred at room temperature for 72-96 hours, until it became homogeneous and had maximum solution viscosity. When necessary, the reaction mixture was diluted with minimal amounts of DMAc, to allow effective stirring with a magnetic stir bar.

The diamine monomers used in this study were: bis[4-(3-aminophenoxy)phenyl] sulfone (mBAPS, 98%, TCI), bis[4-(4-aminophenoxy)phenyl] sulfone (pBAPS, 98%, TCI), 4,4’-diaminodiphenyl ether (DADP, 98%, TCI), and 2,2’-bis(trifluoromethyl)benzidine (TFMB,
98.5%, Akron Polymer Systems). The dianhydride monomers were: bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTDA, 97%, Alfa-Aesar), 4,4’-(hexafluoroisopropylidene)diphenic anhydride (6FDA, 99%, Alfa-Aesar), 3,3’4,4’-biphenyltetracarboxylic dianhydride (BPDA, 98%, TCI), and 4,4’-oxydiphenic anhydride (OPDA, 98%, TCI). These were used as received, without further purification. All of these monomer structures are shown in Fig. 1.

![Molecular structures of the monomers in this study.](image)

We prepared polyimide films suitable for experimental studies by thermal imidization of PAA solutions, using a conventional two-step process summarized schematically in Fig. 2. Each PAA solution was cast onto a glass substrate using a doctor blade technique [10]. The PAA film thickness was controlled by using spacers, resulting in polyimide films with thickness in the range of 50-100 μm. The substrate with cast PAA solution was dried in an oven at 80°C for 3 hours, followed by thermal imidization, first at 200°C for 30 min and then at 280°C for 30 min, in a dry nitrogen atmosphere. We chose these temperatures to be above the imidization temperature, which we had previously confirmed by FT-IR spectroscopy, in order to ensure complete imidization reactions. Free-standing polyimide films were obtained by peeling from the glass substrates, after cutting the edges of the films.

![Schematic representation of polyimide synthesis reactions.](image)

3. Measurement techniques

We measured the refractive indices, \( n \), of free-standing film samples, approximately 50-100 μm thick, with a Metricon Model 2010 prism coupler. This instrument uses a piston to press the film samples against a prism. The instrument was modified by adding heaters to allow temperature-dependent refractive index measurements. Calibrated thermocouples located near the film sample were used to monitor and control temperature. All index measurements were done in a dry nitrogen atmosphere, after each film sample was dried to remove absorbed water. In order to minimize stress-induced effects in the index results, the minimum pressure
needed to achieve coupling of light into the samples was used. The wavelength of 632.8 nm was chosen for these measurements because it is within the region of highest transparency for all of the polyimide films studied here. A fused silica standard was also measured for absolute index calibration.

The accuracy of refractive index measurements on polymer film samples using the Metricon prism coupler was the subject of a detailed discussion in our previous publication [11]. In that work, we noted a distinction between the reproducibility of the measured refractive index values, which can reach $\pm 5 \times 10^{-5}$ after a sufficient number of measurements, and the uncertainty in the absolute index values, which remains at $\pm 2 \times 10^{-4}$. In the present study, our main interest is in the $dn/dT$ values, which are obtained only from differences between index measurements at several temperatures. The uncertainties associated with these index differences, and hence the resulting uncertainties in $dn/dT$, are derived only from the degree of reproducibility and do not depend critically on the absolute index accuracy. To minimize the uncertainties associated with reproducibility, for each sample in this study, measurements of $dn/dT$ were done at 2-4 positions, over 2-4 temperature cycles, covering an area of approximately 10 mm$^2$. Within each temperature cycle, each index measurement was repeated 5-10 times at each temperature. We estimate the uncertainties in our reported $dn/dT$ values to be $\pm 3\%$.

Because no in-plane optical anisotropy was observed in any of these films when placed between crossed polarizers, we assumed these films to be isotropic in-plane [6]. However, the birefringence between the in-plane and out-of-plane directions was measured directly with $s$- and $p$-polarized light, giving $n_{TE}$ and $n_{TM}$ respectively. Generally, $|n_{TE} - n_{TM}|$ was found to be significantly larger than the uncertainty in the index measurements, which was typically $5 \times 10^{-5}$. This birefringence was taken into account when determining the thermo-optic coefficient, $dn/dT$, by setting $n = n_{ave}$, the average refractive index at each temperature, defined as

$$n_{ave} = \sqrt{(2n_{TE}^2 + n_{TM}^2)/3}. \quad (1)$$

Temperature-dependent refractive index measurements were performed between 25°C, slightly above room temperature, and 105°C. Prior to measurements, each sample was kept at 105°C in a dry nitrogen atmosphere in order to remove absorbed water. The lower temperature limit was dictated by our instrument’s lack of cooling capability, while the upper limit was chosen to be significantly below the glass transition temperature for all film samples investigated. This also represents a practical range of temperatures for terrestrial optical applications. At each temperature, the samples were allowed to equilibrate for about 20 min prior to measurement, during which time they were not in contact with the prism in order to allow unrestricted dimensional changes. Although initial index measurements were done at intervals of 10°C, the data showed that $n(T)$ was linear, implying a constant $dn/dT$ over this temperature range. Therefore, the temperature interval was increased to between 20°C and 80°C in later data sets, in the interest of time.

4. Data analysis

Within the scope of this study, there are two fundamental material properties that are of interest because they can lead to thermal dependence in optical devices. These are the refractive index and the linear dimensions. The temperature dependence of the refractive index, known as the thermo-optic coefficient, or $dn/dT$, was determined experimentally as described above. The temperature dependence of the linear dimensions is described by the CTE along the light propagation direction. While the CTE can be measured by various techniques, it can also be inferred from the measured $dn/dT$ values (for an isotropic
material) within the context of the Lorentz-Lorenz model, which has been shown to accurately describe the behavior of optical polymers. In the case of polymers, a reasonable assumption in the Lorentz-Lorenz model is that thermal expansion is the dominant contribution to temperature-dependent changes in the polymer’s dielectric properties, meaning that the temperature dependence of the molecular polarizability may be neglected.

The Lorentz-Lorenz function, $L(T)$, which summarizes the model, can be written as

$$L(T) = \frac{n^2(T) - 1}{n^2(T) + 2} = \left(\frac{\frac{4\pi N_A \alpha}{3 M}}{\rho(T)}\right), \quad (2)$$

where $\alpha$ is the molecular polarizability volume, $\rho(T)$ is the density, $M$ is the molecular weight, and $N_A$ is Avogadro’s number. This form of the Lorentz-Lorenz equation reflects the assumption, mentioned above, that the temperature dependence of the refractive index, $n(T)$, results only from that of the density, $\rho(T)$. In turn, $\rho(T)$ is determined by the material’s VCTE, denoted here as $\beta$, which defines the change in volume, $V(T)$, within a range of temperatures between $T_0$ and $T_1$, as

$$\beta = \frac{1}{V(T_0)} \left(\frac{\Delta V}{\Delta T}\right), \quad (3)$$

where $\Delta T = T_1 - T_0$ and $\Delta V = V_1 - V_0$. This implies

$$\rho(T) = \frac{\rho(T_0)}{1 + \beta \Delta T}, \quad (4)$$

which, using Eqs. (2) and (3), allows us to obtain $\beta$ as

$$\beta \Delta T = \frac{\Delta V}{V(T_0)} = \frac{L(T_0)}{L(T_1)} - 1. \quad (5)$$

Thus, our measured $n(T)$ along with the Lorentz-Lorenz model also allows us to determine $\rho(T)$, and therefore $\beta$.

The above analysis enables a comparison of optical polymers based on their $dn/dT$ or $\beta$ values obtained from $n(T)$ measurements. However, when choosing a polymer for the purpose of manufacturing a thermally-stable optical device, it is not sufficient to compare these material properties individually. This is because the thermal stability of an optical device is generally determined by the combined effects of both refractive index and dimensional changes with temperature. To demonstrate this within the context of a concrete but simple example, we consider the focal length of a single thin lens [12], whose spherical surfaces have radii of curvature $R_1$ and $R_2$. If we neglect thermal changes in the ambient refractive index (namely, air), the focal length, $f$, is given by

$$\frac{1}{f} = (n-1) \left(\frac{1}{R_1} - \frac{1}{R_2}\right). \quad (6)$$
Since temperature-induced changes in $R_1$ and $R_2$ are determined by the material’s LCTE along the propagation direction, which is $\beta / 3$ in an isotropic material, the temperature dependence of $f$ can be calculated from

$$\frac{d\left(\frac{1}{f}\right)}{dT} = \left(\frac{1}{R_1} - \frac{1}{R_2}\right)\left(\frac{dn}{dT} - (n-1)(\beta / 3)\right).$$  \hspace{1cm} (7)

Thus, for this lens example, the fractional change in focal length with temperature is given by

$$\frac{1}{f}\left(\frac{df}{dT}\right) = \left(\frac{\beta}{3}\right) - \left(\frac{1}{n-1}\right)\left(\frac{dn}{dT}\right).$$  \hspace{1cm} (8)

As shown in Eq. (5), the Lorentz-Lorenz model allows us to obtain $\beta$ from the measured $n(T)$. Alternately, the relationship between $dn / dT$ and $\beta$, implied by the Lorentz-Lorenz model (Eq. (2)), can be written explicitly as [6]

$$\frac{dn}{dT} = -\frac{(n^2 - 1)(n^2 + 2)}{6n}\beta.$$  \hspace{1cm} (9)

After substituting Eq. (9) into Eq. (8), this allows us to determine the temperature dependence of the focal length based exclusively on measurements of $n(T)$, which gives an alternative to Eq. (8) for the fractional change in the focal length of the single thin lens as

$$\frac{1}{f}\left(\frac{df}{dT}\right) = -\left(\frac{n^3 + n^2 + 4n + 2}{n^4 + n^2 - 2}\right)\left(\frac{dn}{dT}\right).$$  \hspace{1cm} (10)

5. Results

An example set of $n(T)$ measurements for a free-standing film of mBAPS-BTDA, done at 632.8 nm and in a nitrogen atmosphere, is shown in Fig. 3. The $dn / dT$ value obtained in this case from a linear least-squares fit to the average index is $-107$ ppm/°C, with an estimated uncertainty of ± 3 ppm/°C. Within measurement error, the small birefringence seen in Fig. 3, $|n_{TE} - n_{TM}| \sim 6 \times 10^{-4}$, is independent of temperature in this case, unlike previous results for other polyimides [6].
As described above, we further analyzed the $n(T)$ results to determine the VCTE ($\beta$) within the context of the Lorentz-Lorenz model, according to Eq. (5). This is shown in Fig. 4, which corresponds to the $n(T)$ results for mBAPS-BTDA plotted in Fig. 3. Note that both $L(T)$ and $\Delta V/V_o$ are linear in $T$ over the temperature region investigated here, implying a VCTE of 141 ppm/°C, with an uncertainty of ± 4 ppm/°C. Of course, the linearity of these results implies that the VCTE is constant in this temperature range.

Fig. 3. Measured refractive index, $n(T)$, for mBAPS-BTDA. Solid circles: TE polarization. Open circles: TM polarization. The lines are linear least-squares fits to the data.

Fig. 4. Lorentz-Lorenz function, $L(T)$, calculated from the data in Fig. 3 (circles), and the corresponding change in volume, $\Delta V/V_o$ (triangles), for mBAPS-BTDA. The lines are the respective linear least-squares fits.
We applied this analysis of the $n(T)$ results to the measurements done on all polyimides synthesized for this study. We summarize the refractive index obtained at 632.8 nm and 25°C in Table 1, and the $dn/dT$ obtained between 25 and 105°C in Table 2. The corresponding VCTE values, calculated from the $n(T)$ results using Eq. (5), are shown in Table 3. As a point of reference, we have also measured $dn/dT$ of two common optical polymers, PMMA and polycarbonate, obtaining values of $-116$ ppm/°C and $-130$ ppm/°C, respectively. We discussed our PMMA measurements in detail in our previous publication [11], where we showed our results to be in good agreement with literature values [13,14]. Similarly, our polycarbonate measurements are in good agreement with published VCTE values for this material [15].

### Table 1. Average Refractive Index at 632.8 and 25°C for Polyimides in This Study

| Dianhydride | BTDA | 6FDA | BPDA | OPDA |
|-------------|------|------|------|------|
| mBAPS       | 1.6165 | —    | 1.6823 | —    |
| pBAPS       | 1.6096 | —    | —    | 1.6654 |
| DADP        | 1.5947 | 1.5911 | 1.7193 | —    |
| TFMB        | —    | 1.5429 | 1.6269 | 1.6096 |

### Table 2. $dn/dT$ (ppm/°C) at 632.8 for Polyimides in This Study, between 25 and 105°C

| Dianhydride | BTDA | 6FDA | BPDA | OPDA |
|-------------|------|------|------|------|
| mBAPS       | $-107$ | —    | $-106$ | —    |
| pBAPS       | $-146$ | —    | —    | $-114$ |
| DADP        | $-146$ | $-107$ | $-100$ | —    |
| TFMB        | —    | $-78$ | $-75$ | $-87$ |

### Table 3. VCTE ($\beta$) (ppm/°C) for the Polyimides in This Study, between 25 and 105°C

| Dianhydride | BTDA | 6FDA | BPDA | OPDA |
|-------------|------|------|------|------|
| mBAPS       | 141  | —    | 122  | —    |
| pBAPS       | 197  | —    | —    | 137  |
| DADP        | 203  | 149  | 108  | —    |
| TFMB        | —    | 120  | 97   | 116  |

### 6. Discussion

#### 6.1 Role of thermal expansion

One approach to identifying the polyimide backbone components which lower the VCTE is to note that, in Table 3, the row containing TFMB and the column containing BPDA have the lowest average VCTE. The material with the smallest VCTE is TFMB-BPDA, whose VCTE is $97$ ppm/°C between 25 and 105°C. Furthermore, DADP-BPDA, TFMB-OPDA, and TFMB-6FDA all have smaller VCTE’s than other polyimides in Table 3.

To put these results in perspective, our measured VCTE values in Table 3 can be compared to common optical polymers, such as PMMA and polycarbonate. A typical literature value of VCTE for PMMA is $215$ ppm/°C near 25°C [13,14]. Note that the VCTE of PMMA is temperature dependent, and there is some variation in the reported values. Less variation is observed for polycarbonate, whose VCTE near 25°C is $184$ ppm/°C [15]. By comparison, the VCTE of TFMB-BPDA is about 45% of that of PMMA, and about 60% of that of polycarbonate. We further note that our result for the VCTE of TFMB-BPDA (97
ppm/°C) is smaller than VCTE values previously reported for other optical polyimides, in approximately the same temperature range. Pottiger et al. [7], for example, reported the VCTE’s of several polyimide films ranging from Upilex-S (130 ppm/°C) to Kapton-H (174 ppm/°C) and PI-2450 (192 ppm/°C). More recently, Ishige et al. [8] reported the VCTE’s, derived from X-ray studies, of a set of crystalline polyimide films made by combining nine diamines with PMDA (pyromellitic anhydride), and also by combining four diamines with s-BPDA (3,3,4,4-biphenyltetraarboxylic dianhydride). Their reported VCTE values ranged from 196 ppm/°C to 116 ppm/°C.

In previous studies of polyimide films, a low CTE was commonly associated with simple, rigid-backbone polymer structures. Aromatic polyimides with rod-like shapes typically had lower CTE’s [16]. This correlation was also found in the study of crystalline polyimides by Ishige et al. [8], where the VCTE increased as the number of p-phenylene linkages and p-phenylene ether linkages increased, as well as when bulky side groups were added. Such linkages can lead to a flexible backbone. The smallest VCTE measured in that study (116 ppm/°C) was for the polyimide of PMDA and PPD (p-phenylene-diamine), where this diamine had the simplest rigid structure of those tested.

By contrast, the lowest VCTE’s in the amorphous polyimides reported here were found in nonplanar molecular structures that contain sterically hindered, kinked linkages between phenyl rings. In spite of this, the VCTE’s of these amorphous polyimides are comparable to, or lower than, the VCTE’s of the previously-studied crystalline polyimides. This suggests that the correlation between molecular structure and VCTE for amorphous polyimides may differ from that for crystalline polyimides.

Theoretical treatments of the thermal expansion of polymers usually involve substantial approximations. In a polymer crystal, there are strong covalent bonds along the molecular axis within a chain, and weak van der Waals bonds between chains. One model treats the polymer crystal as a set of quasi-rigid segments held in roughly parallel bundles by the weak inter-chain forces [17]. The thermal expansion is assumed to be dominated by anharmonicity in the vibrations associated with the inter-chain interactions. Wada et al. [18] use this picture to derive an equation for the thermal expansion of a polymer crystal. They consider the vibrations of a simple cubic lattice, in which each lattice point is a segment that represents the moving unit of the inter-chain vibrations. This moving segment is usually associated with a monomer unit of the relevant polymer. Following the Grüneisen equation, they derive an expression for the VCTE ($\beta$) of the crystalline polymer [18] as

$$\beta = \gamma C_{\text{inter}} K,$$  \hspace{1cm} (11)

where $C_{\text{inter}}$ is the inter-chain heat capacity, $\gamma$ is the Grüneisen parameter, and $K$ is the isothermal volume compressibility. They also hypothesize that, since only the low-frequency inter-chain vibrations make a significant contribution to VCTE near room temperature, $C_{\text{inter}}$ should reflect the heat capacity that arises from such inter-chain vibrations. This inter-chain heat capacity is approximated by

$$C_{\text{inter}} = \frac{3k_b\rho}{m'},$$  \hspace{1cm} (12)

where $k_b$ is the Boltzmann constant and $m'$ is the mass of the coherently moving segment of the polymer, which is generally the molecular weight of the monomer unit [18]. Substituting Eq. (12) into Eq. (11) gives

$$\beta = 3k_b\rho \gamma K \left(\frac{1}{m'}\right).$$  \hspace{1cm} (13)
Equation (13) has been found to be reasonably accurate for crystalline materials. For example, Ishige et al. [8] assumed that the Grüneisen parameter was constant and showed that a plot of $\beta/K$ vs. $\rho/m^*$ was reasonably linear for their crystalline polyimides. This implies that, for their set of crystalline polyimides, the variation in VCTE is consistent with the model of Wada et al. [18], which describes VCTE as resulting from anharmonicity in the inter-chain vibrations.

However, as shown in Fig. 5, where we plot our measured VCTE values vs. $1/m^*$, with $m^*$ assumed to be the monomer molecular weight, the situation is different for the set of amorphous polyimides studied here. For the plot shown in Fig. 5, we also assume a constant $\gamma$, as was done in Ref [8], but we further ignore the variations in $\rho$ and $K$ across our polyimides, as explained below.

![Fig. 5. The VCTE ($\beta$) vs. $1/m^*$, where $m^*$ is the monomer molecular weight. The solid points are color coded to identify the dianhydride component of the amorphous polyimides studied here. The black open points are data for the crystalline polyimides previously reported by Ishige et al. [8], along with a corresponding least squares linear fit (black line).](image)

As seen in Fig. 5, the VCTE’s of the amorphous polyimides studied here do not vary linearly or even monotonically with the inverse of the monomer molecular weight. This implies that the model used in deriving Eq. (13) is not appropriate here. Thus, it appears that anharmonicity in the inter-chain vibrations does not account for the VCTE’s of these amorphous materials. Note that the axes in Fig. 5 are slightly different from those of Fig. 11 in Ref [8], where corrections for $\rho$ and $K$ were included. Such corrections were not used here because $\rho$ and $K$ are not known with sufficient accuracy for the amorphous materials. Nevertheless, Fig. 5 is still a valid test of the Wada et al. model [18] because the variation in $m^*$ across these materials is much more significant than the variations in $\rho$ and $K$. For the purpose of comparison to our present results, we include the results of Ishige et al. [8] in Fig. 5. The linear least-squares fit to the results of Ishige et al. [8] demonstrates that the results on crystalline polyimides are well-correlated with $1/m^*$, in agreement with the prediction of the Wada et al. model [18], as found previously [8]. By contrast, Fig. 5 clearly demonstrates that the VCTE’s of our amorphous polyimides are considerably lower than would be expected based on the $m^*$ values, and thus do not follow the description of the Wada et al. model [18].
This is particularly true of the amorphous polyimides represented by the encircled data points in Fig. 5, which are significantly below their crystalline counterparts.

In view of the above results, Fig. 5 implies a significant difference between the mechanisms that contribute to VCTE in crystalline vs. amorphous polymers. This is not too surprising. When a polymer undergoes the phase transition from a liquid to an amorphous glass, excess free volume is incorporated into the glass. The thermal expansion of such a material has contributions from both the thermal expansion of the polymer chains and from the excess free volume (holes) in the material [19]. In the more-disordered amorphous materials, the model of Wada et al. [18], which involves segments held in roughly parallel bundles by the inter-chain forces, becomes less appropriate. In the amorphous case, a disruption of the inter-chain order may reduce the number of inter-chain vibrations that can contribute to thermal expansion, thus lowering the VCTE.

Other processes that have been suggested as contributions to VCTE are associated with structural relaxations. These include local motions of few-atom segments of the polymer chain which persist below $T_g$, the glass transition temperature. Some examples are the well-known $\beta$ transitions, as well as $\gamma$ and $\delta$ transitions, that occur below $T_g$. The contribution of such relaxations was noted in molecular dynamics calculations of thermal expansion in glassy polymers [20]. It has also been noted that side group motions, conformational changes, and localized relaxations, such as crankshaft and membrane vibrations of the main chains, can contribute to VCTE at temperatures above a transition temperature where the motions occur [21,22]. Thus, unlike the case of the crystalline polyimides studied previously, where inter-chain vibrations were shown to contribute significantly to VCTE, our results suggest that structural relaxations may contribute more significantly than inter-chain vibrations to the VCTE’s of our amorphous polyimides.

In the present study, the different dianhydrides and diamines also provide an initial probe of the effect of molecular structure differences on the structural relaxations that determine VCTE. A striking example is seen in the first column of Table 3. Note that the VCTE of mBAPS-BTDA is ~30% smaller than that of pBAPS-BTDA. These two materials are structural isomers that differ only in the positions of the amine group on the phenyl ring. Neyertz and Brown [23] recently reported a molecular dynamics study of the differences between meta and para anhydride-amine links in a polyimide membrane. They found that in amorphous polyimide films the meta-substituted polyimide chains are more tightly coiled than the para-substituted polyimide chains, their void space is slightly smaller, and their mobility is lower. This results in the meta-substituted polyimide having a higher resistance to localized chain motion and a smaller volume expansion upon CO$_2$ sorption. While their interest was in the effect on CO$_2$ sorption, the difference they found in the polyimide secondary structure and its effect on the relaxations is consistent with the difference in VCTE observed here, between the meta- and para- isomers of BAPS. We infer that this difference is caused by the meta-substituted phenyl linkage in m-BAPS leading to a different secondary structure, with fewer contributions to VCTE.

A further example of such effects, also seen in Table 3, is the low contribution of a TFMB component to VCTE, even though it has a rod-like structure and bulky side groups. In this case, steric hindrance due to the ortho-CF$_3$ groups contributes to more disorder in the packing of materials containing TFMB, which prevents closer packing of adjacent polyimide chains, and thus inhibits contributions from phenyl group rotations.

### 6.2 Opto-thermal properties

In order to compare the suitability of these polyimides for the purpose of manufacturing thermally-stable optical devices, we consider the thermal effect on the focal length of a simple optical component, namely a single thin lens. As discussed above, we combine the results for $dn/dT$ and VCTE, shown in Tables 2 and 3, to obtain the fractional change in
focal length with temperature for such a lens, \((1/f)(df/dT)\), according to Eq. (8). The results are shown in Table 4. We consider these to be “benchmark values” for comparison purposes.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Diamine & BTDA & 6FDA & BPDA & OPDA \\
\hline
mBAPS & 221 & — & 196 & — \\
pBAPS & 306 & — & — & 217 \\
DADP & 313 & 231 & 175 & — \\
TFMB & — & 183 & 153 & 182 \\
\hline
\end{tabular}
\caption{(1/f)(df/dT) (ppm/°C) for Polyimides in This Study, between 25 and 105°C}
\end{table}

As seen in Table 4, the lowest benchmark values in this case belong to TFMB-BPDA and DADP-BPDA. These polyimides also have the lowest \(dn/dT\) and \(\beta\) values of those measured here. The next-lowest benchmark values in Table 4 were obtained for the other two polyimides containing TFMB, namely TFMB-6FDA and TFMB-OPDA. However, we also note that our samples of TFMB-BPDA and DADP-BPDA exhibited some birefringence, with \(|n_{xx} - n_{yy}|\) having values of 0.045 and 0.033 at 25°C, respectively. In addition, TFMB-BPDA is the only polyimide in our study whose birefringence is significantly temperature dependent. This is a consequence of \(dn_{xx}/dT\) being different than \(dn_{yy}/dT\) for this material, being \(-80\) and \(-66\) ppm/°C, respectively. While this behavior is not unusual for many polyimides [6,7], it is unique within the group of polyimides studied here. Birefringence and its temperature dependence are known to arise from orientation variations in the molecular backbone, and are likely to vary in magnitude based on processing conditions. However, these effects are beyond the scope of the present study, which focused only on optimizing the backbone structure.

By comparison, we have measured (by the same methods) benchmark values of approximately of 285 and 304 ppm/°C for the widely-used optical polymers polycarbonate and PMMA, respectively. This implies that the TFMB-based polyimides investigated here are nearly twice as thermally stable, in the context of our benchmark, than the most commonly-used optical polymers.

Another point of comparison is fused silica, an important inorganic optical material. We calculate its benchmark value as \(-27\) ppm/°C based on published values of its optical properties [24], which is at least 5 times better than our best polyimides. (The difference in sign is due to the fact that for fused silica, unlike for polymers, the temperature dependence of the polarizability contributes much more to the temperature dependence of the refractive index than the CTE.)

7. Conclusions

We have evaluated the opto-thermal properties of a set of amorphous polyimide films having small or negligible birefringence. Compared to commonly used optical polymers, TFMB-based polyimides had VCTE’s that were approximately half those of PMMA and polycarbonate. The polyimide TFMB-BPDA had the lowest VCTE measured in this study, namely 97 ppm/°C.

Unlike previous studies where low VCTE values in polyimides were associated with rigid linear backbone molecular structures, for the amorphous polyimides in the present study the lowest VCTE values were measured in nonplanar structures with sterically hindered, kinked linkages between phenyl rings. Qualitative considerations and comparison with theory suggest that inter-chain vibrations, which have been shown previously to account for the VCTE in crystalline polyimides with linear backbones, do not represent the dominant
contribution to VCTE in the present amorphous materials. For amorphous materials, contributions from structural relaxations, exemplified by the well-known $\beta$, $\gamma$, and $\delta$ processes below $T_g$, seem to be the more likely contributions to VCTE.

We conclude that amorphous polyimides with favorable backbone structures, like those identified here, are a class of materials that can improve the thermo-optical stability of polymeric optical devices. We note that, for the matrix of materials studied here, the backbone structure was varied but the processing was not optimized for any individual material. Since it has been shown that the VCTE and $dn/dT$ of amorphous polyimides depend on the synthesis procedure and/or post-synthesis processing and annealing conditions [7,25], it is reasonable to suggest that these properties could be improved by optimizing the processing procedures [26].

The logical next step in creating a specific polyimide useful for optical device applications would be to study the effect of processing and annealing procedures on the properties of the amorphous polyimides with the most promising backbone structures, as identified in this study.