Thickness–Direction Thermal-Expansion Measurements

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SYNOPSIS

Thermal expansivity in the thickness direction for three commercially synthesized and processed polyimide films, PMDA–ODA, BPDA–ODA, and BPDA–PDA, have been measured. The expansivity in the thickness direction is significantly higher than that in the in-plane direction. The observed anisotropy is explained by the orientation texture of the films. The differences in the expansivity is explained by the molecular conformation of the chain. The latter is calculated by energy minimization excluding the entropic effects. The conformation analysis reveals a helical-like conformation for ether-linkage-containing chains, which explains the higher expansivity in PMDA–ODA as opposed to BPDA–PDA. The possibility of helical conformation in PMDA–ODA and BPDA–ODA is novel. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Polymers have a unique role in the microelectronics industry as low dielectric packaging materials. High thermal stability, low dielectric constants, and processing compatible to the global packaging building conditions have made polyimides an important class of organic materials. With the complexity and decrease in characteristic dimensions, the need for better physical properties (and their characterization) becomes essential for improved packaging performance and reliability.

A microelectronics package is composed of many materials ranging from thermal expansion coefficients, α, of $\sim$ 3 ppm for silicon to over 30 ppm for organic dielectric. The thermal stress caused by differential thermal expansion makes the thermal expansion coefficient (α) a property of importance in deciding the applicability of a dielectric as a packaging material from a reliability standpoint.

The thermomechanical analyzer (TMA) is the commonly used method to measure α.[1] However, the technique limited to α in the in-plane direction, i.e., α_{x-y}. In this paper, we describe the measurement of the thermal expansivity in the thickness direction,

α_z. The anisotropy measured by this technique is discussed in the light of the orientational order of the film and the chain conformation of the polyimides studied.

EXPERIMENTAL

Three types of commercially available polyimide films were used—Kapton H, Upilex S, and Upilex R—because of their widespread use in the electronics industry. Kapton (from E. I. Dupont de Nemours & Co.) is produced via polycondensation of pyromellitic dianhydride (PMDA) and oxydianiline (ODA). Upilex S (from Ube Industries, Ltd., Japan) is formed via polymerization of biphenyldianhydride (BPDA) and p-phenylene diamine (PDA). Upilex R (also from Ube) is derived from biphenyldianhydride (BPDA) and ODA. For each type, films of nominal thicknesses of 50 and 125 μm were used to determine if the film thickness has an effect in the thickness-direction thermal expansion coefficient. Prior to thermal expansion measurements, the films were cleaned using acetone and isopropyl alcohol and baked at 200°C for several days as in the case of our previous study.[2]

Thermal expansivity in the thickness direction is measured by a sensitive technique that measures the change in thickness as a function of temperature.
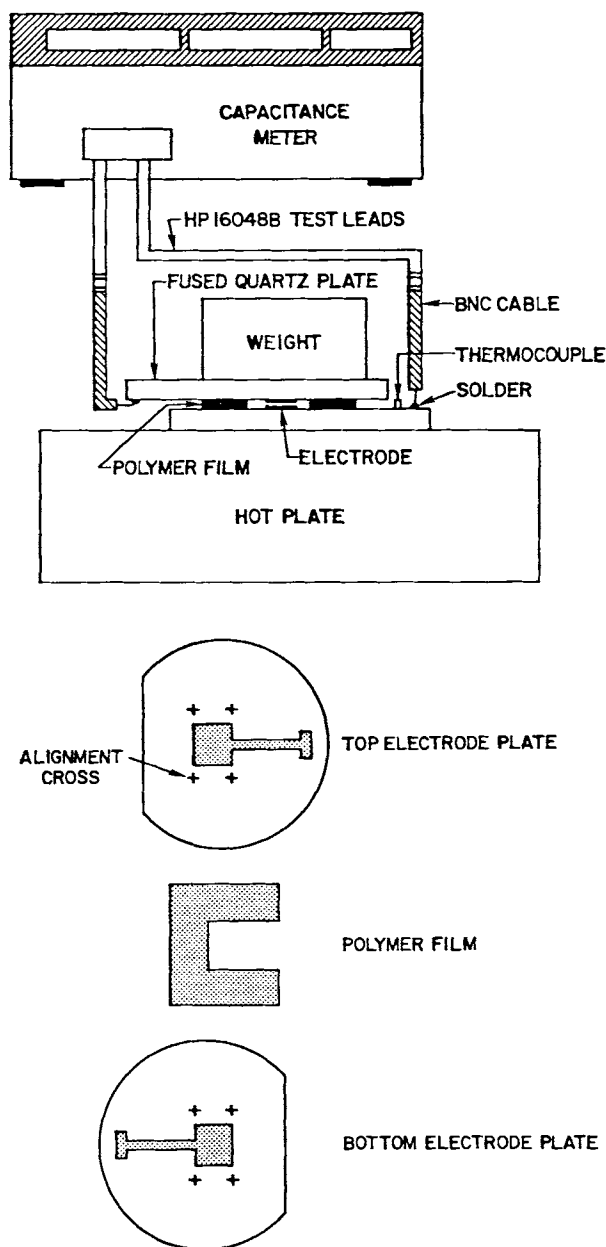
Figure 1 (a) The sample is placed between two fused quartz plates with gold electrodes shown in (b). The polymer film acts as spacer to form a capacitor with an air gap defined by the two electrodes. A weight is placed to ensure good mechanical and thermal contact in the sample assembly and the hot plate. The electrodes are connected to the capacitance bridge. (b) The sample assembly is composed of two gold-coated-fused quartz electrode and a "C"-shaped polymer film sample that circumvents around the square electrodes, acting as a spacer and making a parallel plate capacitor.

Two gold electrodes are vapor-deposited on two separate glass plates. The electrodes form a parallel capacitor with the polymer as a spacer between the glass plates [see Fig. 1(a)]. This sample assembly is placed on a hot plate under a dead weight, with a thermocouple. As the temperature changes, the polymer expands or contracts, changing the air gap between the electrodes. Monitoring the capacitance change, ΔC, as a function of temperature change, ΔT, the α_z can be determined by a simple relation:

$$\alpha_z \simeq \frac{\Delta d}{d\Delta T} \simeq -\frac{\Delta C}{C\Delta T} + 2\alpha' \qquad (1)$$

where d is the thickness of the sample and Δd is the corresponding change in thickness, d, and α' is the effective linear thermal expansion coefficient of the electrode. The latter is measured by using a standard sample of known expansivity. Sephire was used in the present study. The details of this technique are given elsewhere.[2] Using this technique, α_z, of 50 and 125 μm-thick Kapton H, Upilex S, and R films is measured between 50 and 160°C.

RESULTS AND DISCUSSION

Figures 2 and 3 show the capacitance (C) vs. temperature (T) data obtained for a 125 μm-thick Kapton H and Upilex S film: The squares represent data obtained from experiment and the solid line is according to eq. (1) for α_z of 83 and 58 ppm/K, respectively. The α_z corrected for electrode expansion is given in Table I for all the three polyimides tested. The α_z is reasonably independent of the dead weights applied on the sample for good thermal contact and to flatten the film.[2] For other film types and/or thicknesses, the capacitance vs. temperature behaviors are similar, although the data for Upilex R films exhibit irreversibility between the heating and cooling data (Fig. 4). Table I shows the α_z measured by

Table I Thermal Expansivity

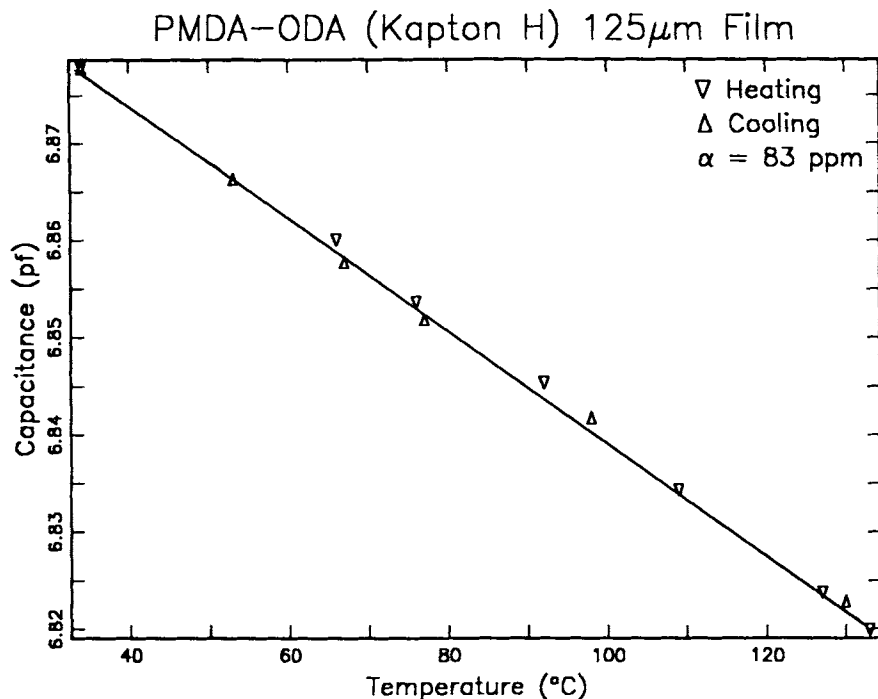| Polymer	Thickness (μm)	Density (g/cc)	Thermal Expansivity		
			α_x	α_y	α_z
PMDA–ODA	50	1.42	20	20	83
	125	1.42	20	20	83
BPDA–ODA	50	1.39	15	15	52
	125	1.39	15	15	61
BPDA–PDA	50	1.47	8	8	51
	125	1.47	8	8	58

PMDA–ODA (Kapton H) 125μm Film

Figure 2   Capacitance vs. temperature for 125 μm-thick Kapton H (PMDA–ODA) film. The straight line is in accordance with eq. (1) corresponding to a total expansivity (including the electrodes) of 82 ppm/°C.
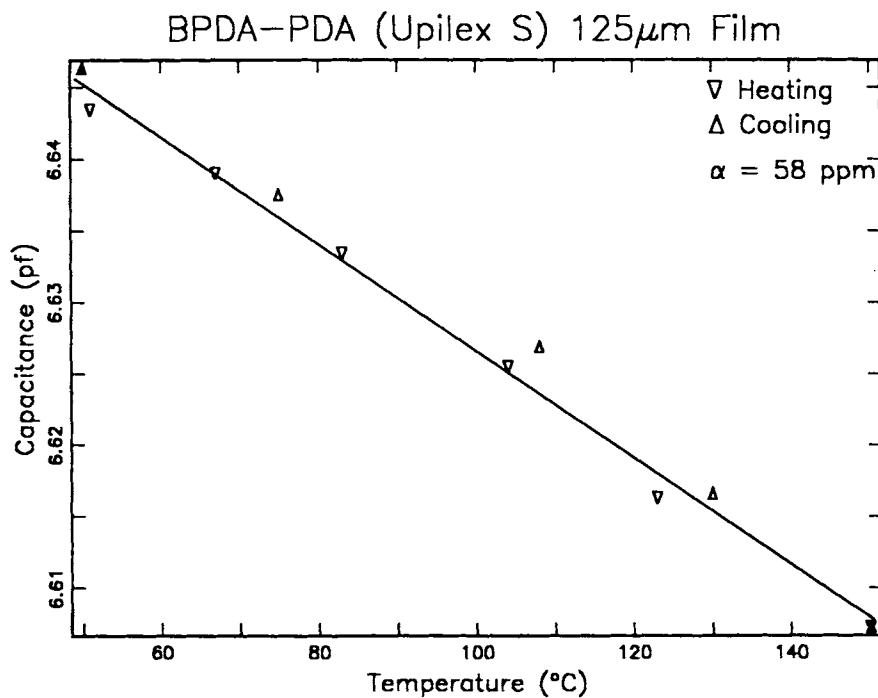
BPDA–PDA (Upilex S) 125μm Film

Figure 3   Capacitance vs. temperature for 125 μm-thick Upilex S (BPDA–PDA) film. The expansivity of the sample assembly from eq. (1) is 57 ppm/°C.

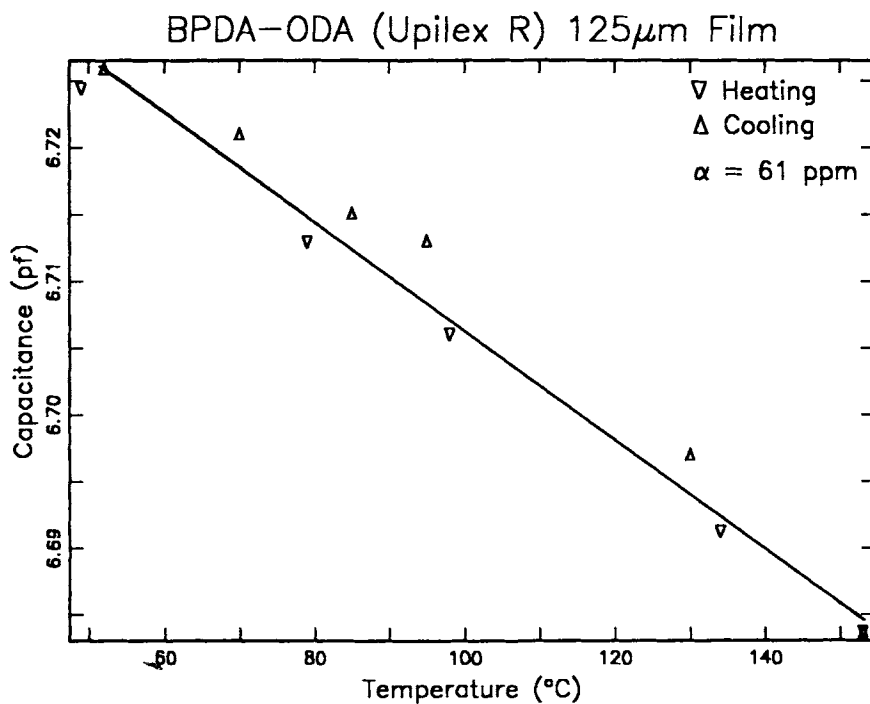## BPDA–ODA (Upilex R) 125μm Film

Figure 4   Capacitance vs. temperature for 125 μm-thick Upilex R (BPDA–ODA) film. Note the variance in the heating and cooling data as compared to Kapton H (Fig. 2) and Upilex S (Fig. 3).
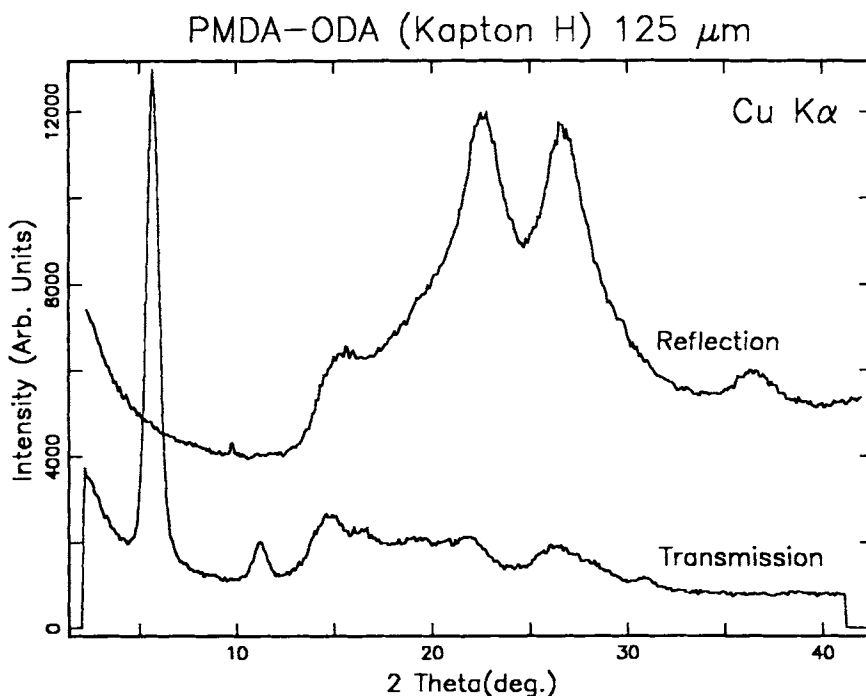
PMDA–ODA (Kapton H) 125 μm

Figure 5   WAXS curve for PMDA–ODA for CuKα at λ = 1.54178 Å. The reflection and transmission mode correspond to a structure perpendicular and parallel to the film surface. The reflections at scattering angle 2θ 5.75° and 11.25° corresponding to momentum vector q ($= 4\pi \sin \theta/\lambda$), 0.408 and 0.795 Å^{-1}, are first-order and second-order reflections along the chain axis.
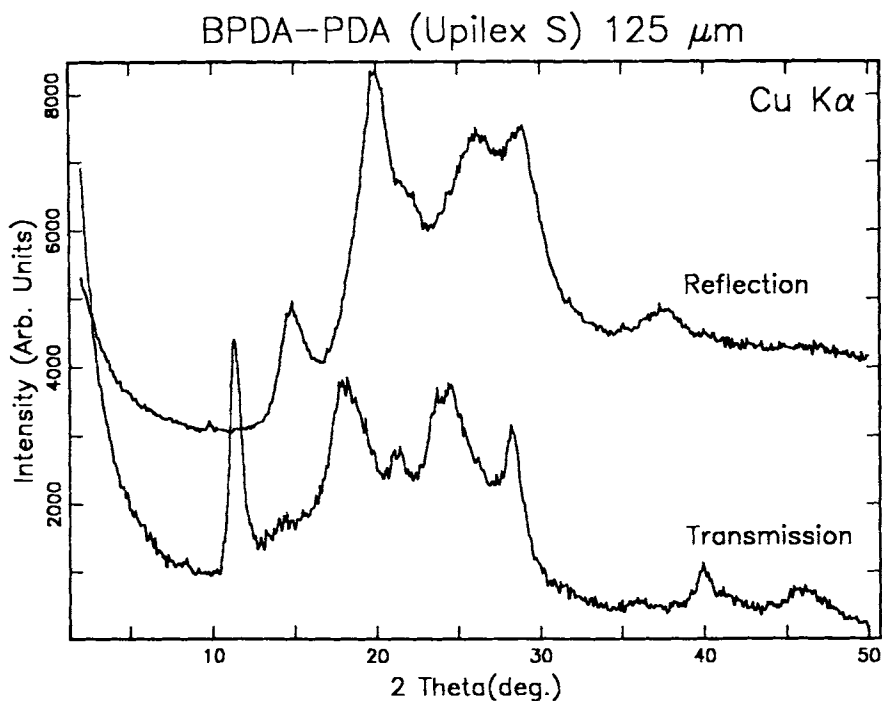
BPDA–PDA (Upilex S) 125 μm

Figure 6   WAXS curve for BPDA–PDA for CuKα at λ = 1.54178 Å. The reflection and transmission mode correspond to a structure perpendicular and parallel to the film surface. The reflection at 2θ = 11.32°, corresponding to q = 0.804 Å^{-1}, is due to periodicity along the chain axis.
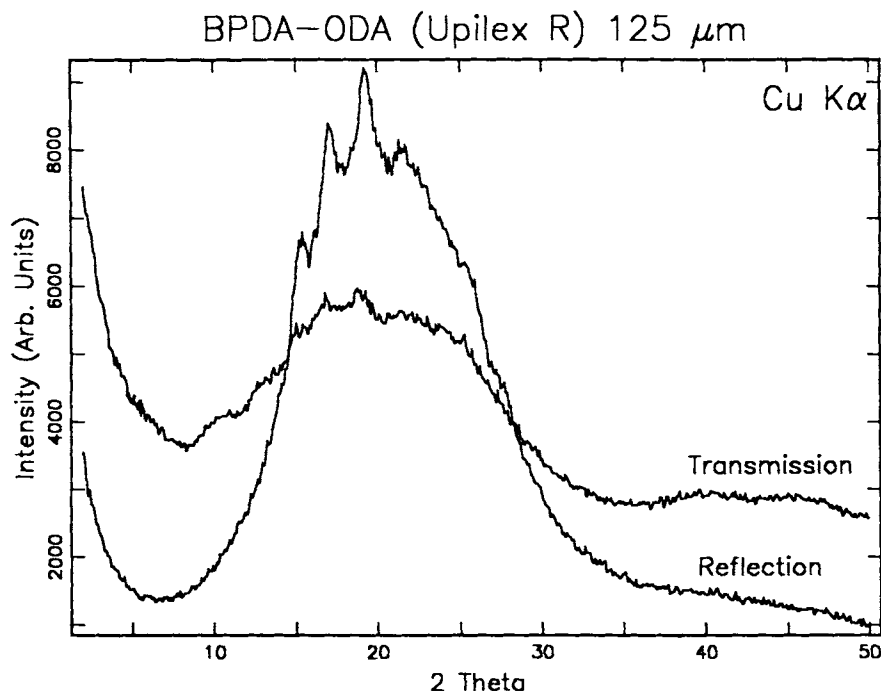
BPDA–ODA (Upilex R) 125 μm

Figure 7   WAXS curve for BPDA–ODA for CuKα at λ = 1.54178 Å. The reflection and transmission mode correspond to a structure perpendicular and parallel to the film surface. There are no reflections corresponding to a structure along the chain [i.e., (001)] and the polymer is more disordered than are PMDA–ODA and BPDA–PDA.
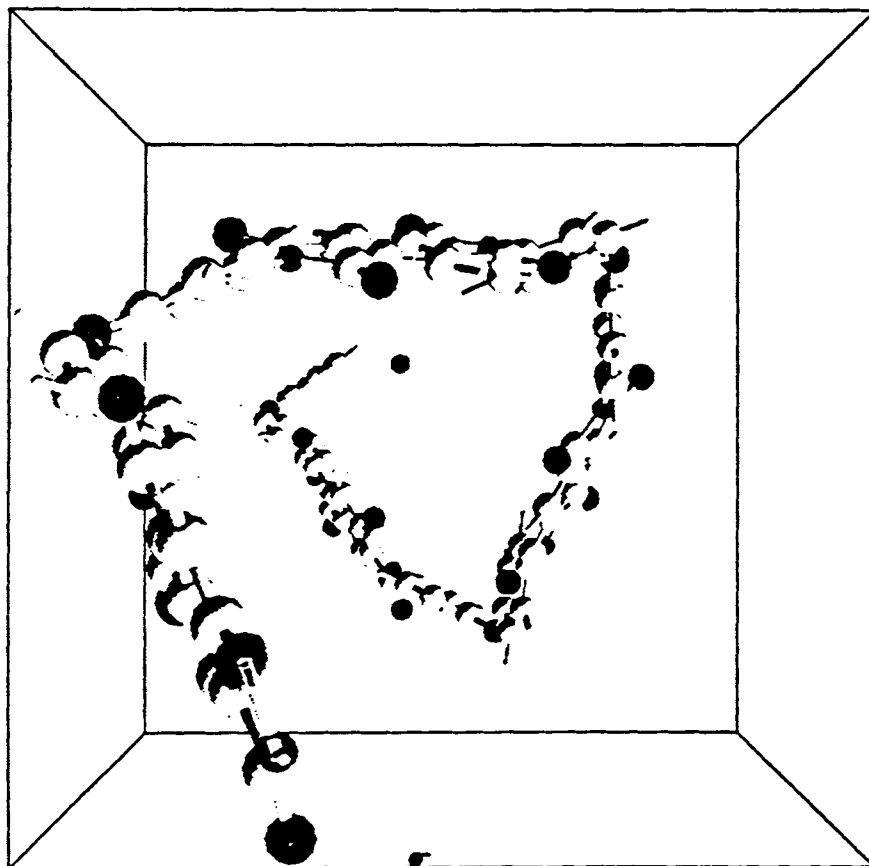
Figure 8 (a), (b), and (c) are the conformations of PMDA–ODA, BPDA–ODA, and BPDA–PDA, respectively, as calculated by program CHARMM at 0 K (i.e., no entropic effects). The conformation is zoomed along the chain axis to indicate the helical structure. The size of the cube for this perspective is 6 × 6 × 20 Å for (a) PMDA–ODA and (b) BPDA–ODA and (c) 18 × 18 × 60 Å for BPDA–PDA. The former form a threefold helix with an oxygen atom at the vertices and the latter is a very low density (i.e., unrealistic) helix indicating a rigid rodlike structure.

the capacitance technique described above. The in-plane expansivity, α_{x-y}, are reported in the literature.[3,4]

The following inferences can be derived from the results shown in Table I:

- The expansivity in the thickness direction, α_z, is significantly different and greater than the x-y plane direction, α_{x-y}.

- The in-plane expansivity, α_{x-y}, for PMDA–ODA and BPDA–ODA are quite similar compared to the corresponding α_{x-y} for BPDA–PDA. The former are within 25%, whereas the latter is $\geq 50\%$ lower.

- The thickness expansivity, α_z, for BPDA–PDA and BPDA–ODA is much lower than α_z for PMDA–ODA.

- The effect of thickness on α_z is more significant in BPDA–PDA and BPDA–ODA than in PMDA–ODA.

The inferences mentioned above are discussed below in the light of wide-angle X-ray scattering (WAXS) data and enthalpic energy minimum (ordered) conformation of a single chain based on the CHARMM computer program.[5]

The anisotropy in the thermal expansivity in the thickness direction, α_z, and the in-plane direction, α_{x-y}, is explained by the texture of the films. WAXS studies on PMDA–ODA reveal a reflection at momentum vector, q = 0.408 and 0.795 Å^{-1}, corresponding to the periodicity along the chain axis (Fig. 5).[6] The presence of the reflection in transmission (i.e., **q** is parallel to the x-y plane) and its absence
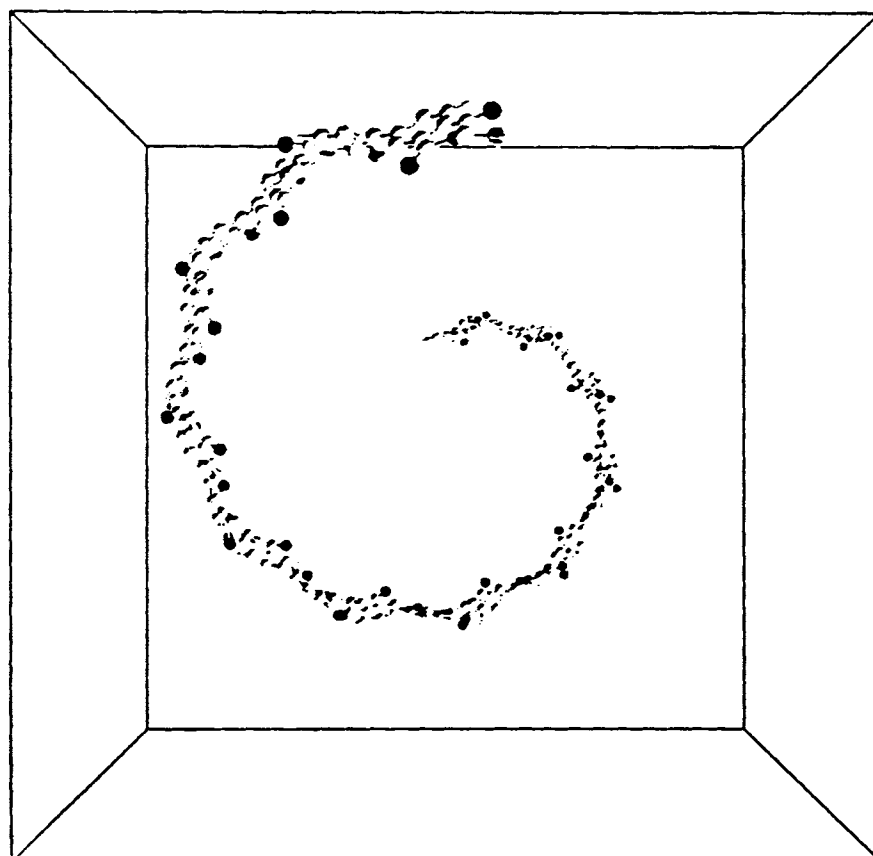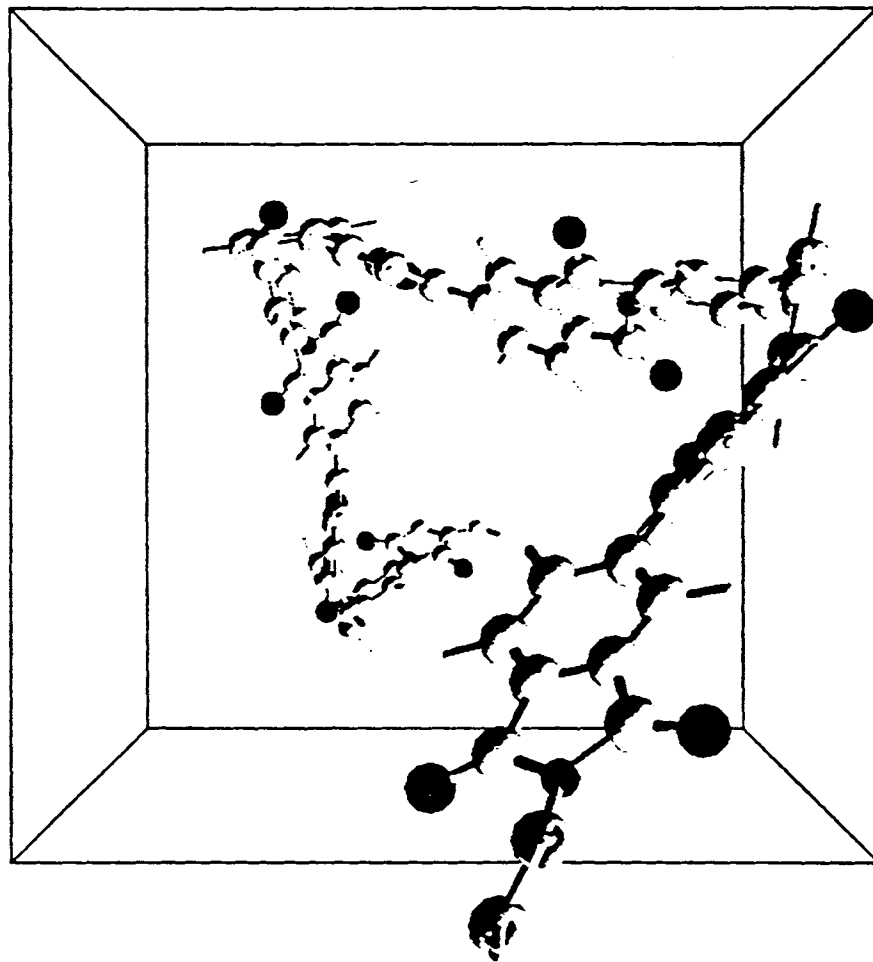
Figure 8 *(continued from the previous page)*

in reflection (i.e., $\mathbf{q}$ is parallel to z-axis) indicate that the molecular chains are parallel to the x-y plane (Fig. 5). Comparing the WAXS in reflection and transmission for Upilex-S reveals a similar result from the reflection at $q = 0.804$ Å^{-1} (Fig. 6). The diffraction pattern for Upilex-R reveals a more disordered structure (Fig. 7). There is no reflection corresponding to periodicity along the chain or pure intrachain reflection. This aspect will be discussed later. However, the reflections in the wider-angle range, corresponding to the interchain packing, are present in reflection and absent in transmission, indicating chain orientation parallel to the x-y plane. This texture is called the planar texture, where the chains are parallel to a plane (x-y plane in the present sample).[7]

The planar texture explains the isotropic expansion in the x-y plane that is different from the expansion along the z-axis. Since the thermal expansion along the chain is lower (even negative for stiff polymers) than in the lateral (i.e., packing) direction, a lower expansivity in the x-y plane is expected.

To explain the differences in the expansivity of the three polyimides, it is important to look at the molecular conformation of the chains in the ordered state. The lowest-energy conformation of an isolated chain at 0 K (i.e., only the enthalpic contribution to the free energy is considered) using the computer software package CHARMM is shown in Figure 8. PMDA-ODA and BPDA-ODA form a 3/1 helix due to the oxygen linkage in the ODA, adding a degree of freedom for the molecule to turn. BPDA-PDA forms a highly expanded helix. Since this is a single-chain calculation, such an expanded helix without any specific strong interaction is unlikely to form in a condensed state at ambient temperatures due to density considerations (i.e., the structure will have low density) (Table II). Nevertheless, the expanded helix does prove the rigid structure of BPDA-PDA. The actual structure may contain segments similar to the helical conformation spaced by either a disordered or different conformation segment.

The thermal expansivity in the x-y plane is due to the properties along the chain axis as indicated

Table II Single-chain Molecular Dimensions

Polymer	Pitch (Å)	Maximum Radius (Å)		
		Oxygen	Nitrogen	Carbon
PMDA-ODA	38	7.13	5.23	7.04
BPDA-ODA	49.5	8.56	6.37	8.23
BPDA-PDA	140	18.54	16.78	18.09

by WAXS above. The PMDA-ODA and BPDA-ODA, due to the ether linkage, form similar conformations (3/1 helix) that are less rigid than BPDA-PDA; the α_{x-y} for the former must be closer compared to the latter. This is in accordance with the observation. Furthermore, the lower α_{x-y} observed for BPDA-PDA can be attributed to its chain rigidity. Thus, the expansivity in the chain direction is essentially dictated by the oxygen linkage in the ODA that contributes to the chain flexibility in an otherwise rigid structure.

The expansivity, α_z, along the z-axis is dependent on interchain packing and interactions. The lowest observed α_z in BPDA-PDA among the three polyimides is attributed to its chain rigidity and, hence, closer chain packing (as indicated by its density shown in Table I). The significantly lower α_z for BPDA-ODA compared to PMDA-ODA is puzzling. The observation may be partly attributed to the processing of the film. The Kapton H (PMDA-ODA) and the Upilex R (BPDA-ODA) films are produced by different vendors by an undisclosed process that involves simultaneous imidization and stretching operations.

The lower measured expansivity in BPDA-ODA as compared to PMDA-ODA may more specifically be attributed to residual stresses that depend on the processing conditions of the films. This also is concurrent with the observed thickness effects in films produced by Ube Industries (BPDA-ODA and BPDA-PDA, Table I) as compared to those produced by DuPont (PMDA-ODA, Table I). Also, at higher thicknesses, where the effect of residual stresses are less, the α_z for BPDA-ODA increases by $\sim 20\%$ toward the α_z for PMDA-ODA films. Furthermore, the irreversibility in the heating and cooling cycle in the BPDA-ODA (Fig. 4) as opposed to PMDA-ODA (Fig. 2) and BPDA-PDA (Fig. 3) may also be attributed to residual stresses.[8]

Based on the calculations involving energy minimization, the conformation of PMDA-ODA and BPDA-ODA exhibits one important difference. Although both the conformations form 3/1 helices with the oxygen atom at the vertices, the asymmetric biphenyl group in the dianhydride for BPDA-ODA imparts a directionality to the chain. In PMDA-ODA, the chain is either a left- or right-handed helix; in BPDA-ODA, the chain may also be up or down. This extra constraint will change the packing of the chain and reduce the order in polymer due to slower kinetics, as confirmed by WAXS (Fig. 7) and lower density (Table I). Such a phenomenon is observed in semicrystalline flexible polymers, e.g., polypropylene and nylons.[9,10]

CONCLUSION

The three polyimides, PMDA–ODA, BPDA–ODA, and BPDA–PDA, have significantly different thermal expansion behavior that may be related to the chain conformation and order and to the processing method. Following are the salient conclusions drawn from this study:

- The thermal expansivity is highly anisotropic, i.e., $\alpha_z \neq \alpha_{x-y}$ for the polimides films tested.
- The isotropic in-plane expansivity, $\alpha_{x-y} > \alpha_z$, and WAXS reveal that the texture of the films are planar where the chains are parallel to the x-y plane.
- The single-chain conformations calculated for PMDA–ODA and BPDA–ODA at 0 K (i.e., only enthalpic contribution to free energy) reveal a helical structure with a triangular chain conformation. The oxygen are at the vertices of the triangle.
- The BPDA–PDA chain forms a large helix, indicating a rigid backbone that may form extended chain-ordered structure.
- BPDA–PDA has the lowest α_z and α_{x-y} among the three polyimides tested. This seems to be consistent with it rigid chain backbone as shown by conformation analysis.
- The most important chemical bond that characterizes the chain conformation and, hence, α_{x-y} (along the chain conformation) in the set of polyimides tested, is the oxygen linkage from the ODA moity. The ether linkage makes the conformation helical in the case of PMDA–ODA and BPDA–ODA.

- The interchain packing for BPDA–ODA requires a greater number of constraints than does PMDA–ODA because the former chain also has an up/down direction. Under similar processing conditions, the former polyimide is less ordered and of lower density.

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