

# **Anisotropic Thermal Properties of Solid Polymers<sup>1</sup>**

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This paper discusses the thermal conduction anisotropy in polymers by reviewing currently available theories and experimental methods for studying oriented polymers. The anisotropic thermal conductivity and diffusivity of oriented polymers originate from the difference between the thermal energy transport mechanisms parallel and perpendicular to their molecules. Recent progress in the development of experimental techniques for studying the thermal conduction anisotropy of polymer films with thicknesses near  $1\ \mu\text{m}$  is discussed in connection with modern microelectronics applications. The data obtained from these techniques are expected to serve for developing sophisticated thermal conduction theories that account for the polymer anisotropy and for performing precise thermal design of organic electronic devices that incorporate highly oriented polymer structures.

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**KEY WORDS:** anisotropy; molecular orientation; polymers; specific heat; thermal conductivity; thermal diffusivity.

## **1. INTRODUCTION**

For many years, polymers have been playing an important role in developing novel manufacturing products. Nowadays, the silicon-based microelectronics industry has begun to pay more attention to the potential of polymer materials as a promising on-chip dielectric material [1] and as an active layer in plastic electronic devices [2]. With this technological trend, there has been a growing interest in the studies of the polymer material properties. The thermal conductivity and thermal diffusivity of polymers are of particular importance because they govern the temperature-rise magnitude and the temporal thermal behavior of polymer-based products.

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Polymers can exhibit significant anisotropy in their thermal conductivity [3–8] and diffusivity [9–12]. This anisotropy can occur even for polymers with an amorphous structure, in which any ordered molecular arrangements cannot be found to a large spatial extent, when the molecular chains are partially oriented [8, 11, 12]. Recent work [8] has shown significant thermal conductivity anisotropy in polymer thin films used for microelectronics applications. These results suggest that precise thermal design of modern polymer-based products needs more careful consideration for the anisotropy behavior of polymer materials. This paper reviews theories and experimental techniques useful for studying the anisotropic thermal properties of polymers. Emphasis is given to the characterization of thin-film polymers, which are most relevant to the emerging technologies in the microelectronics industry. Discussions are made for the dependence of the thermal conduction anisotropy on the orientation of the polymer chains.

## 2. ORIGIN OF ANISOTROPIC THERMAL CONDUCTION IN POLYMERS

It is a notable fact that amorphous phases in a polymer, as well as crystalline phases, exhibit significant thermal conduction anisotropy when the polymer chains are partially aligned with each other. It is because the thermal energy transports more efficiently along the polymer chain, which consists of the strong carbon–carbon covalent bonds, than perpendicular to the polymer chain, where the thermal energy is carried by means of the weak van der Waals interaction of molecules. This behavior is observed for any kind of polymer material, whether crystalline or amorphous.

There are two cases in which significant thermal conductivity anisotropy is introduced to a polymer material: (1) the polymer experiences a mechanical deformation under a stretching force and (2) the polymer is deposited onto a substrate by the spin-coating and curing process to form a film with a thickness of a few micrometers. The macroscopic deformation of polymers can increase the anisotropy because it yields molecular structures that are highly aligned to the draw direction. The orientation of the microscopic structure can yield highly anisotropic thermal conduction properties. In previous studies [3, 5–7, 9–11], the thermal conductivities and the thermal diffusivities of stretched polymers in varying directions were measured and an increase in the anisotropy factor with the degree of material deformation was observed. Figure 1 shows the thermal conductivities of amorphous polymers parallel and perpendicular to the draw direction as a function of the draw ratio,  $\lambda = L/L_0$ , where  $L_0$  is the original length of the solid in the draw direction before it is stretched and  $L$  is the length of the stretched solid in the draw direction.

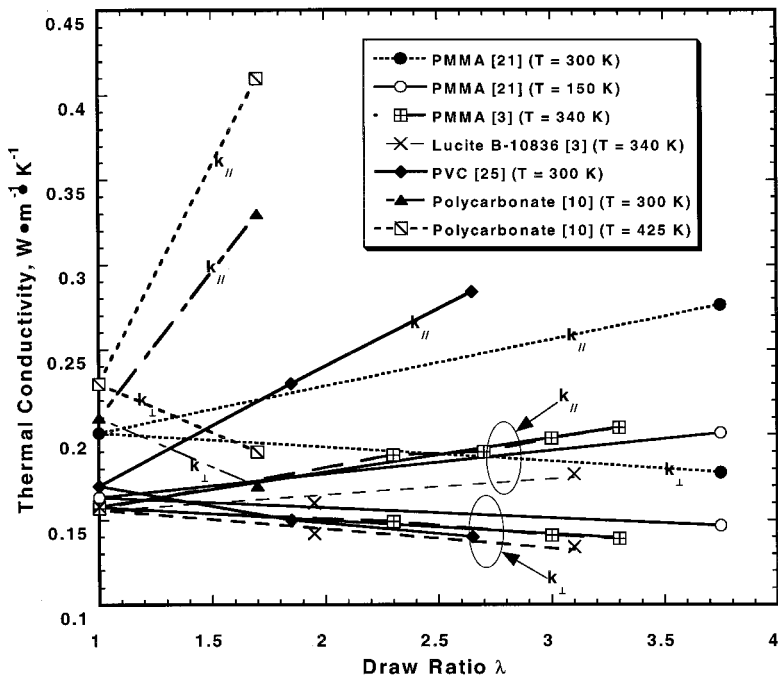


Fig. 1. Thermal conductivity of amorphous polymers as a function of draw ratio  $\lambda$ ;  $\parallel$  and  $\perp$  denote data along and normal to the draw axis of stretched polymers.

Polymer thin films for microelectronics applications are fabricated using spin coating and curing at an elevated temperature. The spin-coating process can cause the polymer chains to be oriented along the in-plane direction of the films due to the centrifugal force during the spinning. The volume contraction of the polymer molecules during the curing process also enhances the alignment of the molecules. A high degree of molecular orientation in the in-plane direction occurs for films of thicknesses of the order of a few microns. This results in significant thermal conductivity anisotropy between the in-plane and the out-of-plane directions. Recent work [8, 13, 14] provided measurements of the thermal conductivity anisotropy in polyimide films, which are shown in Fig. 2.

### 3. MODELS FOR ANISOTROPIC THERMAL CONDUCTION IN POLYMERS

The anisotropy found in polymers can always be related to a statistically averaged orientation of their molecular chains with respect to a

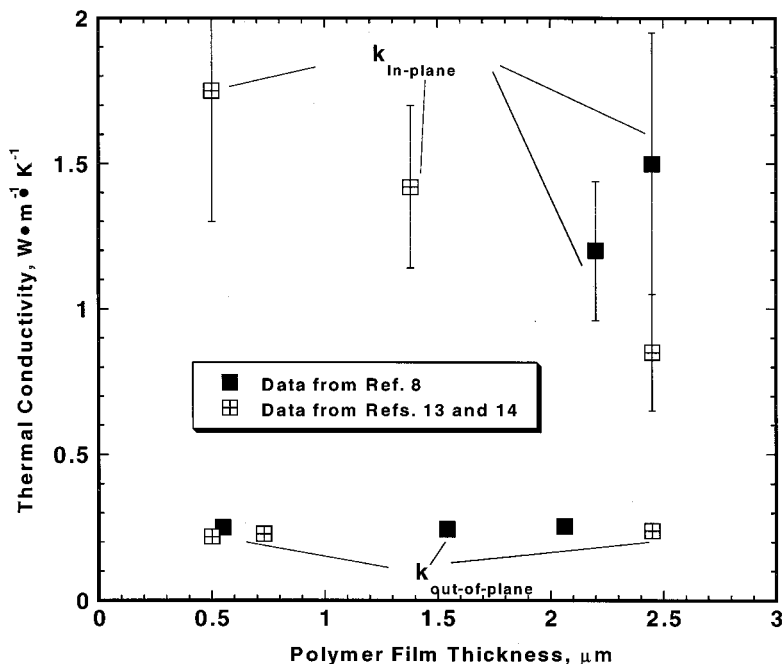


Fig. 2. Thermal conductivity parallel (in-plane) and normal (out-of-plane) to polyimide films as a function of film thickness.

certain reference direction. Henning [15] has proposed a model that views an unoriented polymer as a random aggregate of axially symmetric units whose thermal conductivities are those of the fully oriented materials. The unit can be either a molecular chain segment called a monomer or a local volume unit consisting of perfectly aligned molecular chains. The model assumes that the units would be aligned with their microscopic molecular details unchanged during the deformation of the material. The thermal resistivities of the polymer and the units, which are the reciprocals of the respective thermal conductivities, are given in terms of a tensor of second order. Henning [15] calculated the average thermal resistivity of the polymer by summing all the thermal resistivity tensor elements of the units and dividing it by the total number of the units. This approach is known as the series model [16], which assumes that the total thermal resistance of the material is given by the series of the thermal resistances of the individual units. The theory yields the thermal conductivities of a partially oriented polymer, which are given by

$$\frac{1}{k_{\perp}} = \frac{1}{2} \left[ \left( \frac{1}{k_{\parallel}^u} + \frac{1}{k_{\perp}^u} \right) - \left( \frac{1}{k_{\parallel}^u} - \frac{1}{k_{\perp}^u} \right) \langle \cos^2 \varphi \rangle \right] \quad (1)$$

$$\frac{1}{k_{\parallel}} = \left( \frac{1}{k_{\parallel}^u} - \frac{1}{k_{\perp}^u} \right) \langle \cos^2 \varphi \rangle + \frac{1}{k_{\perp}^u} \quad (2)$$

where  $k_{\perp}$  and  $k_{\parallel}$  are the macroscopic thermal conductivities of the polymer along and perpendicular to the draw direction,  $k_{\parallel}^u$  and  $k_{\perp}^u$  are the thermal conductivities of the basic unit along and perpendicular to the symmetry axis,  $\varphi$  is the angle between the symmetry axis and the draw direction, and  $\langle \cos^2 \varphi \rangle$  is the average of  $\cos^2 \varphi$  for the entire units of the aggregate. In a viscoelastic deformation, the macroscopic deformation is not so simply related to the microscopic deformations. By assuming that the viscoelastic deformation consists of an elastic deformation followed by the viscous flow and that the orientation of the basic unit is associated with the elastic deformation, previous work [17] has calculated  $\langle \cos^2 \varphi \rangle$  as a function of the draw ratio  $\lambda$ . Calculations using Eqs. (1) and (2) performed by Henning [15] are found to be in good agreement with experimental data for polyvinylchloride (PVC). However, in spite of the success of the series model in the derivation of these equations, there is no *a priori* reason why the theory cannot use the parallel model, which assumes uniform a temperature gradient throughout the aggregate. For general polymer materials, the series and parallel models determine only the lower and upper bounds for the actual values of the thermal conductivity, respectively [16, 17].

Choy [18] indicates that the anisotropy behavior of semicrystalline polymers, which consists of crystalline and amorphous phases, varies with the volume ratio of the crystalline phase. Kilian and Pietralla [9] indicate that for semicrystalline polymers under a large deformation, the stress causes local melting and crystallization in the microstructure, which helps increase the heat conduction anisotropy. These results add more complication to the modeling of semicrystalline polymers. The model needs to account for the evolution of the microstructure as well as the variation of the molecular orientation during the deformation. This validates existing models [9, 19] only for relatively small deformations with  $\lambda < 10$ . Further improvements need to be made for the theoretical studies of highly stretched semicrystalline polymers.

Kurabayashi and Goodson [20] have adapted the theoretical approach of Henning [15] to predict the thermal conductivity anisotropy in spin-coated polyimide films. The key parameters in their model are the intrinsic thermal conductivities  $k_1^c$  and  $k_2^c$ , which are governed by the van der Waals interaction of atoms perpendicular to perfectly aligned polymer chains and by covalent bonding of atoms along these chains, respectively,

and the angle  $\phi$  from the in-plane direction of the film. Assuming that the coupling between neighboring chain molecules does not depend on their orientation and that these molecules contribute independently to the heat flow, the model derives the anisotropy factor  $A$ , given by

$$A = \frac{k_{\text{in-plane}}}{k_{\text{out-of-plane}}} = \left[ \left( 1 + \frac{k_2^c}{k_1^c} \right) - \left( 1 - \frac{k_2^c}{k_1^c} \right) \langle \cos^2 \phi \rangle \right] / 2 \left[ \left( 1 - \frac{k_2^c}{k_1^c} \right) \langle \cos^2 \phi \rangle + \frac{k_2^c}{k_1^c} \right] \quad (3)$$

where  $k_{\text{in-plane}}$  and  $k_{\text{out-of-plane}}$  are the in-plane and the out-of-plane thermal conductivities, respectively. Using data from Ref. 8, the model shows that the anisotropy factor could increase to a value larger than 10 for polyimide films with a film thickness decreasing to submicrometers. An important limitation of this model is that heat transport is assumed to be governed only by local chain orientation in the film, without any dependence on the nature or extent of polymer cross-linking. The presence of polymer cross-linking, which is found in many thermosetting polymers, may strongly improve conduction between chain segments separated by tens of nanometers within a given film and render the present localized approach inappropriate.

#### 4. ANISOTROPIC HEAT CONDUCTION MEASUREMENT METHODS

The techniques for studying the anisotropic heat conduction in stretched polymers of relatively large thickness (more than a few millimeters) have been available since the 1960s. The simplest method uses hot and cold plates attached to both ends of a polymer slab. Measuring the applied steady-state heat flux and the temperature gradient across the sample with a thermocouple allows measurement of the thermal conductivity along the slab. Eiermann and Hellwege [21] prepared polymethyl methacrylate (PMMA) polymer samples sliced parallel and perpendicular to the direction of stress and measured both  $k_{\parallel}$  and  $k_{\perp}$  for draw ratios  $\lambda$  up to 4 using this method. Washo and Hansen [3], Henning and Knappe [22], and Hansen and Berier [23] also performed similar measurements for polystyrene (PS), PMMA, and polyethylene (PE). Although the steady-state method is relatively easy to implement, one must expect large experimental uncertainties due to the radiative/air conduction heat loss from the side walls of the sample.

The thermal characterization of anisotropic thin films faces unique experimental challenges. When the steady-state method is applied for studying thin films of thicknesses less than a few millimeters, the thermal contact resistances between the plate and the film sample and between the thermocouple and the plate are comparable to the thermal resistance due to the sample volume. Since these contact resistances are highly unknown, the steady-state characterization yields significant uncertainties. To reduce these uncertainties, Choy et al. [10] employed a transient method called the flash radiometry technique for samples with a thickness of less than  $150\ \mu\text{m}$ . They irradiated a laser pulse on the front surface of the sample and monitored the thermal radiation from the rear surface as a function of time using an infrared detector instead of a thermocouple. This approach allows measurement of the thermal diffusivity  $\alpha$  normal to the film, with which the thermal conductivity  $k$  of the polymer can be extracted using

$$k = \rho C_p \alpha \quad (4)$$

where  $C_p$  and  $\rho$  are the specific heat and the density of the polymer, respectively. It is found that the heat loss due to radiation and air conduction is negligible for measurement of the thermal diffusivity normal to thin films.

Another important issue concerning thin film characterization is that the anisotropy occurs between the directions normal and parallel to the films. This necessitates a method that allows one to measure the thermal conductivities in both of these directions. Table I summarizes recently developed experimental methods for the anisotropy characterization of thin polymer films. Choy et al. [11] have characterized both in-plane and out-of-plane thermal conduction behaviors for biaxially stretched poly(ethylene terephthalate) (PET) films with thicknesses down to  $4\ \mu\text{m}$  using the experimental setup shown in Fig. 3. To study the in-plane thermal conduction in the films, they flashed a line-shaped laser beam on the surface of the film at a right angle to its length and monitored the time-dependent temperature variation at a point in the direction parallel to the film plane. Using this approach, Choy et al. observed that the in-plane thermal conductivity of biaxially stretched PE film could be as high as  $40\ \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at a draw ratio of 350. This thermal conductivity value is about three times higher than that of steel. But in this method, the data analysis for extracting the in-plane conductivity still requires careful consideration of the effect of radiation and air conduction on the measurement because the temperature detection point is located relatively far ( $> 1\ \text{mm}$ ) from the heated region. Considerable heat loss due to radiation and air conduction occurs before the thermal diffusion along the film reaches the temperature detection point.

**Table I.** Summary of Experimental Techniques for Characterizing Heat Conduction Anisotropy in Polymer Thin Films

Technique	Measured conductivity	Experimental setup	Uncertainty	Remarks	Ref. No.
Flash radiometry	$k_{\parallel} (\alpha_{\parallel})$ $k_{\perp} (\alpha_{\perp})$	Fig. 3	6–8% ( $k_{\parallel}$ ) 5–10% ( $k_{\perp}$ )	<ul style="list-style-type: none"> <li>• High accuracy</li> <li>• Analytical solution available for data analysis</li> </ul>	11
Steady-state Joule heating & electrical resistance thermometry	$k_{\text{out-of-plane}}$	Fig. 4	Less than 5%	<ul style="list-style-type: none"> <li>• High accuracy</li> <li>• Simple data analysis</li> <li>• Low radiative/air conduction loss</li> </ul>	8
Harmonic Joule heating & electrical resistance thermometry	$k_{\text{in-plane}}$ ( $\alpha_{\text{in-plane}}$ )	Fig. 5	15%	<ul style="list-style-type: none"> <li>• Numerical calculation needed for the data analysis</li> <li>• Low radiative loss</li> </ul>	8
Harmonic Joule heating & optical thermometry	$k_{\text{in-plane}}$ ( $\alpha_{\text{in-plane}}$ ) $k_{\text{out-of-plane}}$ ( $\alpha_{\text{out-of-plane}}$ )	Fig. 6	30% ( $k_{\text{in-plane}}$ ) 8% ( $k_{\text{out-of-plane}}$ )	<ul style="list-style-type: none"> <li>• Simple sample fabrication</li> <li>• Low radiative/air conduction loss</li> <li>• Tedious data extraction</li> <li>• Large experimental uncertainties</li> </ul>	14

Kurabayashi et al. [8] have recently developed experimental techniques for measuring the thermal conductivity anisotropy in polymer films of thicknesses near  $1 \mu\text{m}$  that are spin coated onto a silicon substrate. The out-of-plane conductivity is isolated using steady-state Joule heating and electrical-resistance thermometry in a microfabricated metal/polymer/metal mesa as shown in Fig. 4, which resembles multilevel interconnection in integrated circuits. The principle is similar to that of the steady-state method, which characterizes the anisotropy of bulk polymers using hot and cold plates. This method uses metallic bridges as a heater and a thermometer, which are patterned using the lithography technique. The advantage of the use of the lithographically patterned structure is that it yields a much lower thermal contact resistance between the bridge and the sample



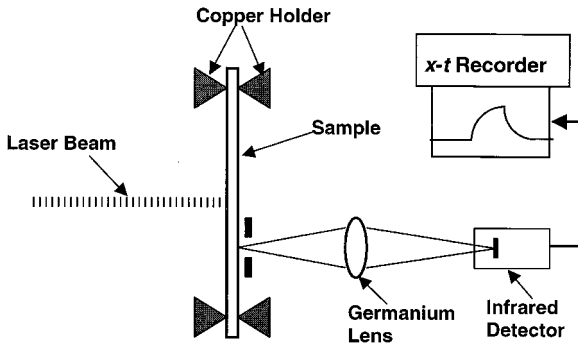


Fig. 3. Experimental setup of the flash radiometry technique for measuring the in-plane thermal diffusivity of PET films [11]. The out-of-plane diffusivity is also measured by aligning the infrared optics with the optical path of the heating laser.

film than the thermal resistance due to the volume of the sample itself. The in-plane thermal conductivity is measured using a free-standing polymer membrane on which a metallic heater/thermometer bridge is patterned. Figure 5 illustrates the structure used for in-plane conductivity measurement, which is fabricated using bulk silicon micromachining. The measurement procedure adapts those used in the  $3\omega$  method [24]. Transient Joule

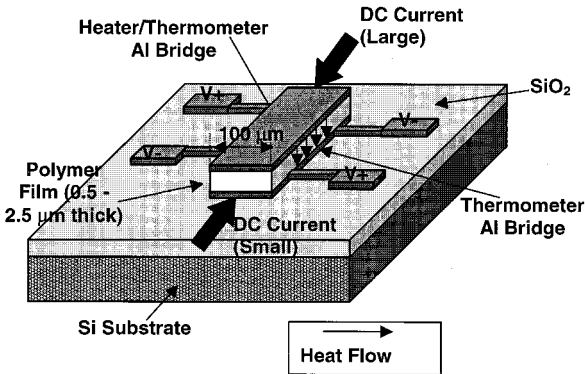
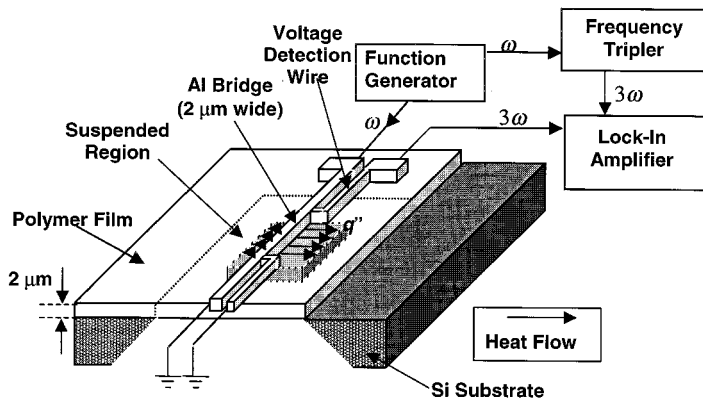


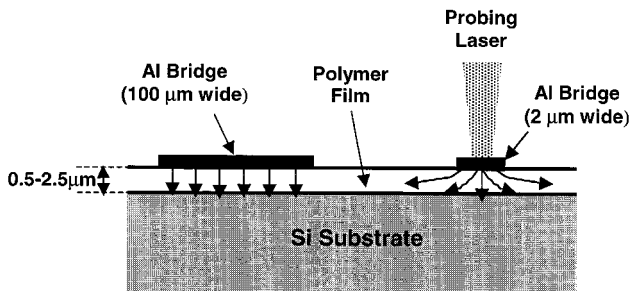
Fig. 4. Schematic of the metal/polymer/metal micromesa structure for measuring the out-of-plane thermal conductivity of polyimide films [8]. The top bridge is sustained by a relatively large DC current ( $\sim 0.1$  A) and generates Joule heat. The resistances of the top and bottom bridges are calibrated as functions of temperature and precisely measured using the four-point probe method.



**Fig. 5.** Schematic of the suspended membrane structure for measuring the in-plane thermal conductivity of polyimide films [8]. The heating frequency applied to the metallic bridge is varied between 1 and 6 kHz.

heating is sustained in the metallic bridge by means of a harmonic electrical current at angular frequency  $\omega$ . Measuring the third component ( $3\omega$ ) of the AC voltage across the metallic bridge with a lock-in amplifier, one can obtain the amplitude of the temperature oscillations at the bridge. The in-plane thermal conductivity is extracted from analyzing the transient temperature responses at frequencies varying between 1 and 6 kHz with the specific heat data of the polymer. In this frequency range, the thermal conductance due to the radiation from the sample surface is calculated to be three orders of magnitude smaller than the conductance along the film. Therefore, the radiative loss is negligible in this method when the measurements are performed in vacuum.

Ju et al. [14] also have measured the thermal conductivity anisotropy in polymer films using the structure shown in Fig. 6. In their method, harmonic Joule heating is induced in metallic bridges which are lithographically patterned with varying widths. The temperature responses in these bridges are monitored using optical thermometry to extract the in-plane and out-of-plane conductivities. The temperature response in the wide bridge ( $>100\ \mu\text{m}$  wide) is governed by the heat conduction normal to the film, whereas the lateral spreading of heat within the film significantly influences the temperature response in the narrow bridge ( $\sim 2\ \mu\text{m}$  wide). This approach does not require the demanding sample preparation processes used in the above work [8] and consequently avoids potential damage to the samples during the processing. Although the experimental uncertainties in the in-plane conductivity measurement are relatively high



**Fig. 6.** Schematic of the structure with Al bridges of varying widths for measuring the thermal conductivity anisotropy between the in-plane and the out-of-plane directions of the sample film [14]. The temperature oscillations at the Al bridges are detected by measuring the reflectivity changes of the metal surfaces.

(about 30%), the fewer difficulties associated with the sample preparation represent a significant advantage of this technique. Using this method, Ju et al. [14] have obtained data for benzophenone tetracarboxylic dianhydride 4,4'-oxydianiline (BTDA-ODA) polyimide films of varying thicknesses, which show that the anisotropy factor lies between four and six and favors lateral conduction as shown in Fig. 2.

## 5. CONCLUSIONS

Anisotropic heat conduction in polymer materials originates from the orientation of their molecular chains. The existing theories succeed in describing quantitatively the anisotropic thermal transport phenomena to some extent. However, more sophisticated models need to be developed to explain fully the relationship between molecular structure and anisotropic behavior for various kind of polymers. With emerging technologies such as plastic-based microelectronics and organic microelectromechanical systems (MEMS), the thermal characterization of polymer thin films with a thickness of a few micrometers becomes more important for precisely studying heat transfer in future electronic devices and solid-state transducers. The precise characterization of polymer thin films requires the measurement of both in-plane and out-of-plane thermal conductivities. The experimental techniques reviewed in this paper may well serve this purpose. Further theoretical and experimental work is necessary to understand the impact of material processing conditions such as deformation rate, spin-coating speed, and curing temperature on the thermal conduction anisotropy in polymer materials.

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