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THERMAL CONDUCTIVITY ANALYSIS OF POLYMERIC CRYSTAL BY MIRAGE EFFECT

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Abstract

Photothermal Techniques are based on the conversion of the modulated light energy into heat within the sample. Using the Photothermal Probe Beam Technique, where the analysis of a laser beam deflected by the mirage effect near the sample leads to the thermal properties of this sample, we have determined the three components of the thermal conductivity tensor of an orthorhombic polydiacetylene single crystal. A numerical simulation of the probe beam deflection is also presented and compared to the experimental data.

Keywords: mirage effect, photothermal techniques, polydiacetylene

Introduction

Different methods have been used to analyze thermal properties of polymers: the "flash" method [1], or the "steady-state potentiometric" technique [2]. The technique used in this study is the photothermal probe beam deflection (or "mirage effect"). It was first introduced by Boccara *et al.* [3], and has since been used in the study of optical [4] and thermal properties [5] of materials.

In such a technique, the sample under study is illuminated by a modulated light beam (pump beam). As a result of radiationless processes, absorbed light is then converted into heat, which induces thermoelastic waves in the sample. For low frequency modulation range (a few Herz) it may be assumed that the contribution of the acoustical mode can be neglected, and so, only the thermal one contributes to the thermal field. The heat flow within the sample produces a refractive index gradient in the adjacent air medium, close to the sample surface. A second laser beam (probe beam) directed through the heated region is deflected by the "mirage effect". The analysis of this deflection leads to the thermal properties of the sample.

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The sample under study is a molecular single crystal of substituted diacetylenes which undergoes a solid-state polymerization under UV, X-ray or electron irradiation [6] according to the reaction:

$$n(R-C\equiv C-C\equiv C-R')\rightarrow(=\overset{R}{\overset{|}{C}}-C\equiv C-\underset{R'}{\underset{|}{C}}=)_n. \qquad (1)$$

Due to the one-dimensional nature of the fully conjugated backbone of the polymer, this crystal exhibits a large degree of anisotropy in its electrical and optical properties [7, 8].

We present in this paper, the determination of the anisotropic thermal properties of polydiacetylene with butoxycarbonylmethylurethane (4BCMU) substituents, where the side groups R and R' are identical to

$$R=R'=-(CH_2)_4-O\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-CH_3. \qquad (2)$$

We can notice for this polymer the presence of CONH units in the side group R, which form hydrogen bonds between neighbouring side group, and so, ensure the rigidity of the polymeric chains.

For this crystal, the unit cell has an orthorhombic geometry and belongs to the spatial group *Pmab*. There are two polymer chains per unit cell, extending in the crystallographic $\vec{c}$ direction. In the Table 1, we can indicate the values of the three crystallographic parameters.

Table 1 Values of the crystallographic parameters of poly-4BCMU [9]

Crystallographic axis / nm	*a*	*b*	*c*
poly-4BCMU	5.375	1.099	0.488

In this note, we present a comparison between numerical simulation and experimental data which leads us to determine the values of the three thermal conductivity coefficients of a 70 μm thick poly-4BCMU sample.

Theory

The geometry used for the theoretical analysis is presented in Fig. 1. In this reference frame, the thermal field $T(u, v, z, t)$ is determined according to the energy conservation law by the 3D thermal conduction equation in an anisotropic medium [10]:

$$\bar{\bar{\kappa}}\nabla^2 T(u,v,z,t) + g(u,v,z,t) = \rho C_p \frac{\partial T(u,v,z,t)}{\partial t} \quad (3)$$

where ρ and C_p are respectively the density and the specific heat of the sample. The quantity $g(u,v,z,t)$ denotes the thermal energy deposited by the pump beam per unit time and unit volume. The second order thermal conductivity tensor $\bar{\bar{\kappa}}$ is expressed in the orthorhombic case as:

$$\bar{\bar{\kappa}} = \begin{pmatrix} \kappa_c & 0 & 0 \\ 0 & \kappa_b & 0 \\ 0 & 0 & \kappa_a \end{pmatrix} \quad (4)$$

where κ_c, κ_b denote the thermal conductivity coefficients respectively parallel and perpendicular to the chains direction, and κ_a perpendicular to the chains plane.

The same equation can be written in the surrounding media, with $g(u, v, z, t)=0$ as they do not absorb the incident light. The stationary solutions

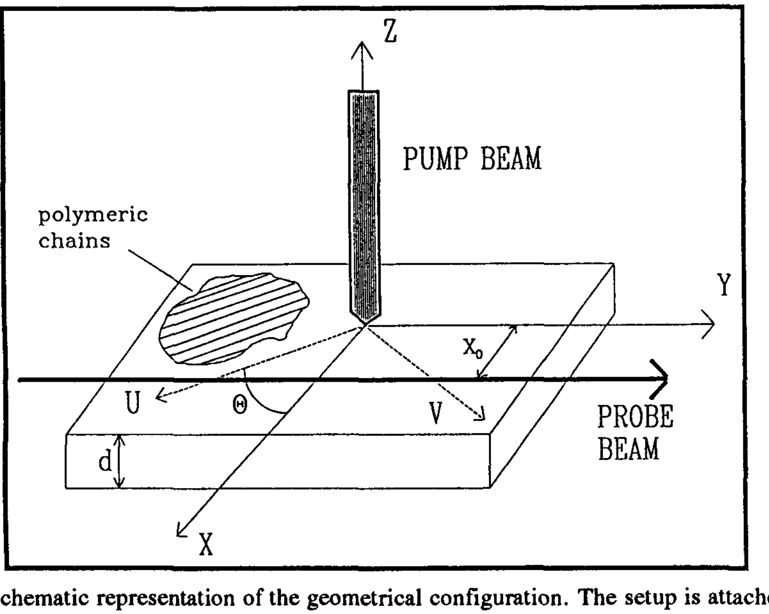

Fig. 1 Schematic representation of the geometrical configuration. The setup is attached to the (X, Y, Z) axis. The probe beam, directed along Y, scans in the X direction. The (U, V, Z) frame refers to the crystallographic ($\vec{c}$, $\vec{b}$, $\vec{a}$) axis. The angle ($\vec{c}$, X) is noted θ

of this differential equation lead to the spatial solutions $\tau_i(u, v, z)$ of the temperature $T(u, v, z, t)$ for a frequency modulation f. Index $i=s$ will refer to the sample medium, $i=g$ to the front gas medium and $i=b$ to the backing one, as defined on Fig. 2.

To determine the temperature distribution in the surrounding probed gas, we used a 2D Fourier transform in the (u,v) plane, taking into account the boundary conditions at the interface (continuity of temperature and heat flow) between the sample and the surrounding atmosphere. In the case of the front configuration, we have obtained the expression of τ_g (Eq. 4, Ref. [11]); in the same way, we can deduce τ_b for the rear configuration case.

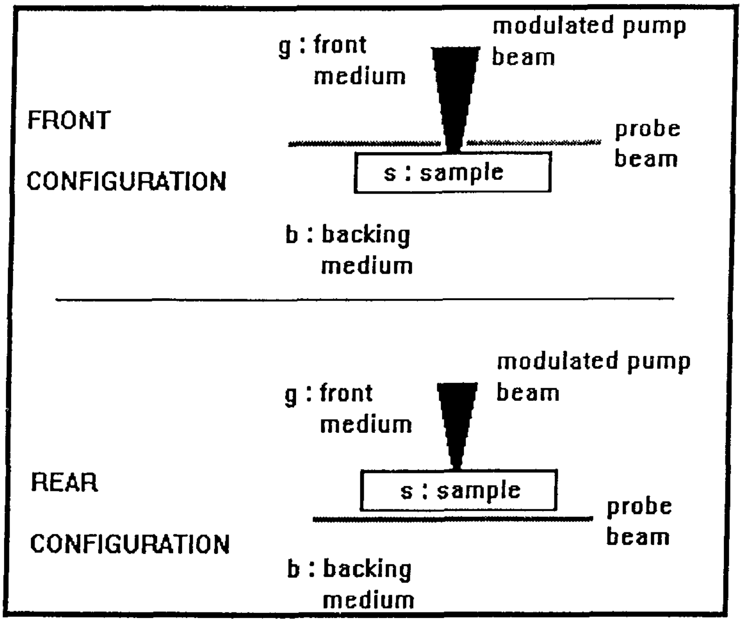

Fig. 2 Front and rear experimental configurations. The pump beam is always directed through the front medium

The magnitude and direction of the probe beam deflection Θ are determined by the periodic gradient of the temperature in the air and are given by the line integral:

$$\vec{\Theta} = -\frac{1}{n}\frac{dn}{dT}\int_L \vec{\nabla}\tau_g \times \vec{dl} \qquad (5)$$

where n is the refractive index for the gas, L is the probe beam path in the interactive region and $\vec{dl}$ is an incremental distance along L. This deflection leads to a normal component Θ_n perpendicular to the surface, and to a transverse one Θ_t parallel to the surface. These components are given by:

$$\Theta_n \propto \int_{-\infty}^{+\infty} \frac{\partial \tau_i}{\partial z} dy \text{ and } \Theta_t \propto \int_{-\infty}^{+\infty} \frac{\partial \tau_i}{\partial x} dy \tag{6}$$

where $i=g$ for the front configuration, and $i=b$ for the rear one.

We will deduce the thermal conductivity coefficients in the chains plane $((\vec{b}, \vec{c})$ plane), from the amplitude of Θ_t *vs.* the distance X_o between the probe and the pump beams, in the front configuration, because of the greater experimental sensitivity observed.

In the direction perpendicular to the chains plane, the value of the thermal conductivity coefficient κ_a can be deduced from the analysis of the highest frequency experiments, when the sample, from thermally thin, becomes thermally thick [11]. It is also possible to obtain the value of κ_a from the study of the amplitude of Θ_n in the rear configuration, for low frequency modulations such as the sample remains thermally thin. Then, for $X_o=0$, the logarithm of the amplitude of Θ_n is actually proportional to the inverse of the square root of the modulation frequency f, as long as the pump beam radius is larger than the thermal diffusion length in the chains plane (the thermal diffusion length μ is equal to $\sqrt{\kappa/\rho C_p \pi f}$), and the sample is very opaque to the incident light.

Results and discussion

Experimental setup

The setup is schematically represented in Fig. 3. The beam of a 8 mW power Argon laser (Ion Laser Technology 5490 A), tuned on 488 nm wavelength, is focused on the sample surface. Assuming a Gaussian profile, the $1/e^2$ spot-light radius measured at the focalization point is about 360 μm. The scanning of the offset X_o is monitored by a 0.1 μm step-by-step motor (Micro-Control). The probe beam is a 2 mW power unpolarized He-Ne laser beam (Melles Griot). The deflection angle (about 10^{-5} radians) was detected by a photoelectric position sensor (Centronic QD 50) and measured by the use of a lock-in amplifier (PAR 5206).

Experiments

All experiments are performed at room temperature, on a 70 μm thick sample weighing 0.6 mg. Front and backing media are both normal atmosphere.

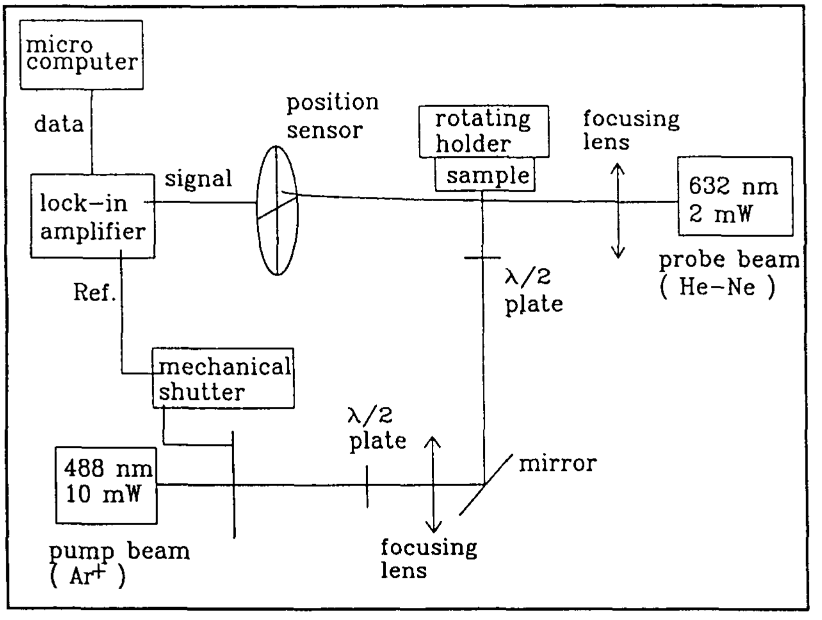

Fig. 3 Block diagram of the experimental setup. Experiments were performed at room temperature on a 70 μm thick poly-4BCMU single crystal.
The chain direction is detected owing to the strong optical dichroïsm and matched with the pump beam polarization by the use of a half-wave plate

Measurements of κ_θ in the chains plane

We represent in the Fig. 4, the plot of the transverse amplitude Θ_t *vs.* the offset X_o in the chains direction, in the front configuration and in the case of a modulation frequency from 0.5 to 10 Hz. For different values of the angle θ , using a half-wave plate, we keep the polarization of the incident beam parallel to the chain axis. So we can notice that all the experiments were performed on an optically opaque sample. The values of the thermal conductivity κ_θ obtained are reported in Table 2.

Measurement of κ_a

In the front configuration, the value of κ_a has been deduced from the analysis of the cross-over from the lowest to the highest frequency experiments (Fig. 4), when the sample, from thermally thin, becomes thermally thick [11]. This thermal conductivity coefficient has been found equal to 0.03 $W\cdot m^{-1}\cdot K^{-1}$.

Table 2 Anisotropic thermal conductivity behaviour in the chain plane of poly-4BCMU

Angle θ / degree	0	15	25	35	45	60	75	90
κ_θ / W·m^{-1}·K^{-1}	2.2 (κ_c)	2.2	1.8	1.6	1.3	0.8	0.65	0.4(κ_b)

On another hand, in the rear experimental configuration, the measurement of the slope of ln(Θ_n) *vs.* $1/\sqrt{f}$ leads to a value of κ_a equal to 0.04 W·m^{-1}·K^{-1}. This method may be more affected by the presence of local defaults, which may explain the difference between the two different values.

Conclusions

We have shown that photothermal probe beam deflection is of interest for the study of anisotropic thermal properties. This technique requires only a few amount of sample and has the great advantage to be contactless. Experiments and numerical simulation are in good agreement and lead to the determination of the thermal conductivity tensor in an orthorhombic crystalline sample.

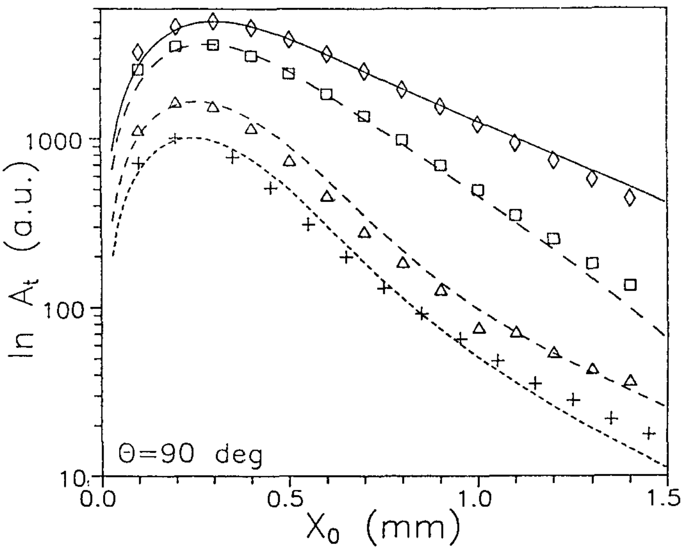

Fig. 4 Plot of the logarithm of the transverse amplitude Θ_t for different modulation frequencies: (◊) for 0.5 Hz, (□) for 1 Hz, (Δ) for 4 Hz and (+) for 10 Hz, which represent experimental data. Solid and dashed lines were computed (eq. 10 ref. [11]) for each frequency

The thermal conductivity tensor of our 4BCMU sample exhibits a large anisotropic behaviour at room temperature, following the anisotropy of the unit cell. The large difference between κ_c and κ_a may be explained by the lamellar structure of this polymer crystal which can be easily cleaved along the chains plane.

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Zusammenfassung — Fotothermische Techniken basieren auf der Umsetzung der modulierten Lichtenergie in Wärme innerhalb der Probe. Durch Anwendung der Fotothermischen Prüfstrahltechnik, bei der die Auswertung eines durch den Luftspiegeleffekt nahe der Probe abgelenkten Laserstrahles zu den thermischen Eigenschaften dieser Probe führt, bestimmten wir die drei Komponenten des Wärmeleitfähigkeitstensors eines orthorhombischen Polydiacetylen-Einkristalles. Es wurde auch eine rechnerische Simulation der Prüfstrahlablenkung durchgeführt und mit den experimentellen Daten verglichen.