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Molecular Orientation and Dielectric Anisotropy in Polyimide Films As Determined by the Microwave Method

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ABSTRACT: Molecular orientation and dielectric anisotropy of polyimide films was studied by the microwave method. The average direction and degree of orientation of the main chains were in good agreement with those determined by the conventional methods utilizing the mechanical breaking and the polarized infrared absorbance. The results gave a definite evidence for the usefulness of the microwave method to study the correlation between the mechanical and high-frequency dielectric properties and molecular orientation of polymer films.

Introduction

Aromatic polyimides exhibit excellent thermal resistance as well as good mechanical and electric properties. Thus, the films have been used as heat-resistive dielectric material for electronic devices such as motor, printed circuit board, electric cable, and integrated circuit board. In the practical application to the electronic engineering field, for example, the information on thermal shrinkage and dielectric properties at microwave frequencies is important. As for polyimide films, the molecular orientation has been estimated from the data on viscoelastic modulus and X-ray diffraction,[1,2] and the complex dielectric constant has been determined only at audio frequencies.[3,4] But the measurement process involved there is rather time-consuming. And the microwave dielectric data on polyimide films has not yet been reported in the literature.

Recently, we have developed a new approach, called the microwave method,[5−23] instead of methods such as X-ray diffraction, infrared dichroism, and mechanical breaking strength. The microwave method makes it possible to measure quickly and accurately the molecular or fiber orientation and the high-frequency complex dielectric constant of sheet materials without contact. It has been applied to paper sheets,[5,6,11,12] polymer films,[7,9,13−15,18−22] blood vessels,[10] cow skins,[16,17] and nonwoven fabrics.[8]

The present paper uses this method to estimate the molecular orientation and the microwave dielectric anisotropy in polyimide films and compares the result with those obtained through the measurements of mechanical breaking strength and polarized infrared absorbance.

Experimental Section

Samples. Test films mainly used here were cut out of commercially available polyimide Kapton 100H (DuPont) film (26 μm thick) that was prepared by the cast method. A uniaxially stretched polyimide film was also used for determining whether the infrared bands are parallel or perpendicular to the stretching direction of the film.

Measurement of Orientation Pattern. A given film mounted in the sample holder is inserted into a narrow free space between a pair of rectangular waveguides constituting the cavity resonator system.[7,9,23] Its block diagram[7,23] is shown in Figure 1. A polarized microwave of frequency f from the oscillator is incident perpendicularly to the plane of the film and at the same time the film is rotated at a speed of 6.0 s/turn about the axis normal to it. Intensities of the transmitted microwave (I) are detected by the detector at every 1° of rotation angle θ, the controller part regulates the rotation angle, and the data accumulated in the CPU give by a computer system the result on a CRT as a polar graph after 30 s and are recorded on a chart. This graph is hereafter called the orientation pattern. For convenience, θ is measured counterclockwise from the machine direction (MD), which is defined as that for rolling films in the process of preparing the films.

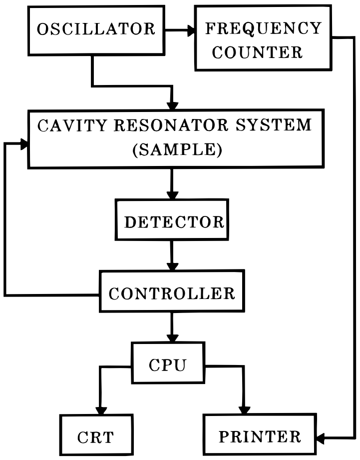

Figure 1. Block diagram of the cavity resonator system for determining the molecular orientation and the dielectric anisotropy by use of microwaves.

The resonance curve in the cavity resonator system before and after insertion of a sample is shown in Figure 2. The insertion of the sample makes the resonance frequency shift to a low-frequency side and reduces the peak height of the resonance curve. I is expressed as[7]

$$I(\theta) = I_{io}(\theta)/\{1 + Q_i^2(\theta)[f_{io}(\theta)/f - f/f_{io}(\theta)]^2\} \qquad (1)$$

Here, I and I_{io} (i = 1, 2) are the transmitted microwave intensities at a given frequency f and a resonance frequency

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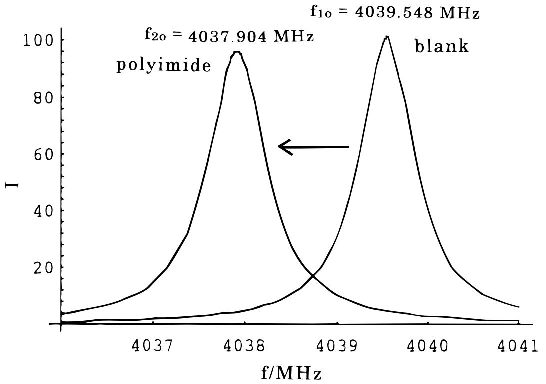


Figure 2. Resonance curves defined as the frequency dependence of the transmitted microwave intensity at a fixed rotation angle before and after insertion of a polyimide film 26 μm thick in the cavity resonator system. The resonance frequencies before and after the insertion of the film are 4039.548 and 4037.904 MHz, respectively.

f_{io}, respectively. Q_i is the ratio of the resonance frequency f_{io} to the half-width Δf_i of the resonance curve ($Q_i = f_{io}/\Delta f_i$). Here, the resonance frequency is defined as the frequency at the maximum of the transmitted microwave intensity in the resonance curve. All these quantities are functions of rotation angle θ at $i = 2$. The subscripts $i = 1$ and 2 indicate the values calculated before and after the insertion of the sample.

For the system with an inserted sample a frequency F was selected so that the transmitted intensity was just half the intensity at the resonance frequency f_{2o}. Then the orientation pattern[15] was measured at F by rotating the sample. Although F varies with the species and thickness of the sample, the variation is very small: the F's for all chosen films are, in general, close to 4.0 GHz. Therefore, in the present study, 4.0 GHz is referred to as the measuring frequency for the orientation pattern data presented below.

Dielectric Measurement. According to the perturbation theory,[24] if a dielectric sheet material is so thin compared with the cavity that the frequency shift caused by it is much smaller than the resonance frequency for the empty cavity, its complex dielectric constant ϵ^* ($=\epsilon' - j\epsilon''$) at θ is calculated from[23]

$$\epsilon^*(\theta) = 1 - [[\omega_2(\theta) - \omega_1(\theta)]/\omega_2(\theta)][2\int_{V_c}|E_1|^2\,\mathrm{d}V/\int_{V_s}|E_1||E_2|\,\mathrm{d}V] \quad (2)$$

where ω is the complex angular frequency, E is the electric field in the cavity, V_c is the volume of the cavity, V_s is the volume of the sample, and the subscripts 1 and 2 refer to before and after insertion of the sheet. It can be shown that the shift of ω due to the presence of the sheet is related to the corresponding shifts of the real frequency f and the Q value by

$$[\omega_2(\theta) - \omega_1(\theta)]/\omega_2(\theta) = [f_{2o}(\theta) - f_{1o}(\theta)]/f_{1o}(\theta) + (j/2)[1/Q_2(\theta) - 1/Q_1(\theta)] \quad (3)$$

For a sufficiently thin sheet it follows from these relations that dielectric constant ϵ' and dielectric loss ϵ'' at θ can be calculated from[9,15]

$$\epsilon'(\theta) = 1 + A(c/t)[f_{1o} - f_{2o}(\theta)]/f_{2o}(\theta) \quad (4)$$

$$\epsilon''(\theta) = B(c/2t)\{[1/Q_2(\theta)] - [1/Q_1]\} \quad (5)$$

Here, t is the thickness of the sample, c is a parameter related to the depth of the rectangular waveguide, and A and B are constants associated with the apparatus. f_{1o} and Q_1 are constants independent of θ.

ϵ' and ϵ'' are measured as follows. The sample direction is fixed to the predetermined rotation angle, where the resonance frequency is searched by tuning the microwave frequency. The f_{io} and Q_i obtained from the resonance curves shown in Figure 2, the sample thickness t, and the parameter c are substituted into eqs 4 and 5. The process is repeated before ($i = 1$) and after ($i = 2$) the insertion of sample. The time needed for dielectric measurement was 30 s at a fixed direction. For the measurement we used a transverse electric wave of the type TE_{10L}, with L = odd integer, as the electromagnetic mode.[9] The sample size was 100 × 100 mm.

Measurements of Mechanical Properties. Strips of 10 mm wide, 50 mm long, and 26 μm thick were cut along the various directions (relative to the MD) from the original film, and the elastic modulus E and the breaking strength BS were measured at a stretching rate of 50 mm/min by use of an INTESCO universal testing machine. The measurement was made for three strips for a fixed direction, and the data were averaged.

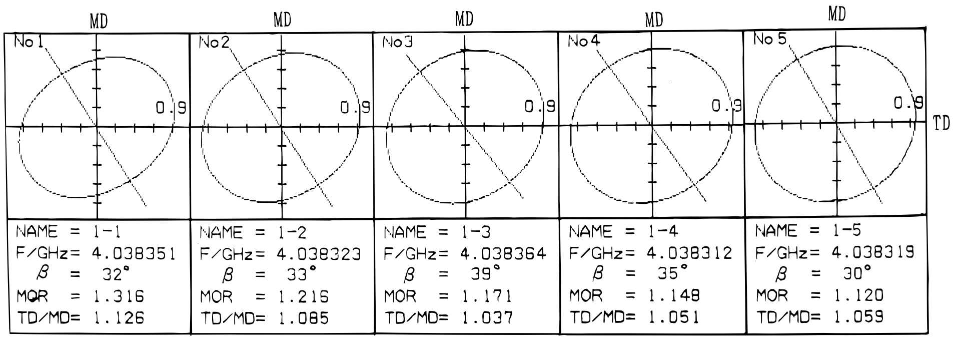
Polarized Infrared Measurement. Polarized infrared rays were perpendicularly incident to the plane of the uniaxially stretched polyimide film. The spectra were measured at the directions parallel and perpendicular to the draw direction. The absorbance at a fixed wavenumber of 435 cm^{-1} was detected at different rotation angles of the original film.

All the measurements were carried out at 25 °C and 65% relative humidity (RH).

Results

Figure 3 gives the orientation patterns measured at 4.0 GHz for polyimide films of 100 mm × 100 mm size (sample nos. 1-1 to 1-5) that were obtained by cutting the original Kapton 100H film (508 mm wide) differently along the TD, where TD means the direction perpendicular to the MD. The F reflecting the film thickness[8] changed little with changing position of the film. This suggests that the film thickness is almost the same in the whole TD. To discuss the orientation characteristics, two parameters are introduced. One is the orientation angle β defined as the θ at which the transmitted microwave intensity I shows a minimum, and the other is the molecular orientation ratio (MOR) defined as the maximum-to-minimum ratio of I. The β relates to the direction of molecular orientation, and the MOR increases with the increasing degree of molecular orientation.[7] These can be taken as the average direction of molecular chains and a measure of orientational anisotropy, respectively. The β changes with changing position and is largest for sample film 1-3, while the MOR decreases with changing position from left to right and is the largest for the sample film 1-1. Thus, two parameters change independently of each other. The ratio of transmitted microwave intensity in the TD to MD is denoted by TD/MD. This ratio is a little different from that for the MOR. But the difference is not so large at various positions and the orientation patterns suggest a possibility that the molecular chains are slightly oriented in the direction deviated by 30−40° from the MD of the film, as likely seen in the biaxially stretched poly(ethylene terephthalate), PET, film.[15]

Figure 4 shows the angular dependence of ϵ' and ϵ'' for the film 1-1 measured at 4.0 GHz. Its elliptic shape indicates weak dielectric anisotropy. Close inspection reveals that both ϵ' and ϵ'' are the largest at θ = 35°, implying that, on an average, the polymer chains in the sample film 1-1 are a little preferentially inclined by this angle from the MD, since the change in dipole moment due to the molecular motion of polyimide is largest in the direction of maximal ϵ''. The angular dependence of ϵ'' also suggests that the maximal-to-minimal ratio of ϵ'' must be a direct measure of the



NAME = 1-1	NAME = 1-2	NAME = 1-3	NAME = 1-4	NAME = 1-5
F/GHz= 4.038351	F/GHz= 4.038323	F/GHz= 4.038364	F/GHz= 4.038312	F/GHz= 4.038319
β = 32°	β = 33°	β = 39°	β = 35°	β = 30°
MOR = 1.316	MOR = 1.216	MOR = 1.171	MOR = 1.148	MOR = 1.120
TD/MD= 1.126	TD/MD= 1.085	TD/MD= 1.037	TD/MD= 1.051	TD/MD= 1.059

Figure 3. Orientation patterns at 4.0 GHz for Kapton 100H films of 100 × 100 mm size that were cut at different positions of the original film of 508 mm wide and 26 μm thick. Dotted lines indicate minimum intensities.

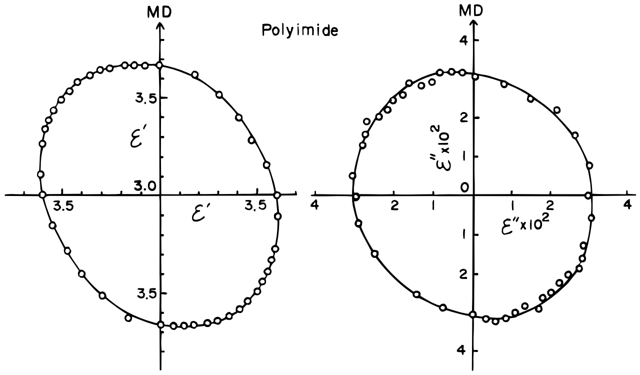


Figure 4. Angular dependence of dielectric constant ϵ' and dielectric loss ϵ'' at 4.0 GHz for the polyimide film 1-1.

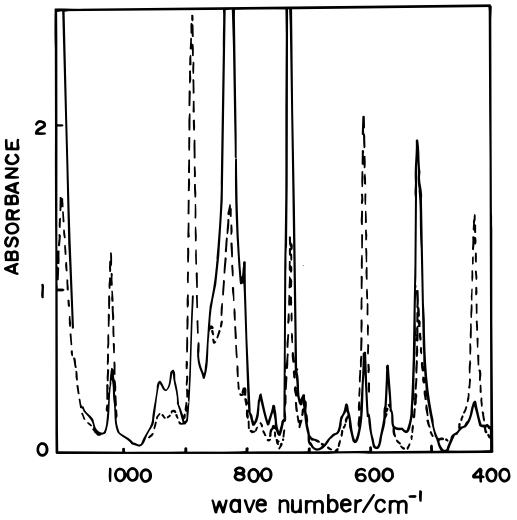


Figure 5. Polarized infrared spectra of a uniaxially stretched polyimide film: (—) the electric vector of the incident infrared beam perpendicular to elongation; (- - -) the electric vector of the incident infrared beam parallel to elongation.

anisotropy[20] due mainly to the molecular orientation of the polyimide. The absolute values of 3.5−3.7 of ϵ' at 4.0 GHz for polyimide films are somewhat larger than those of 3.0−3.5 for PET film at the same frequency;[9,15] the same is true of ϵ'', i.e., 0.030−0.035 for polyimide and 0.015−0.023 for PET.[9,15]

To determine whether the observed infrared bands are parallel or perpendicular ones, then, we measured the polarized infrared spectra for the uniaxially stretched polyimide film (see Figure 5). The infrared spectra of the highly oriented polyimide film indicate that the absorption band at 435 cm^{-1}, for example, has a clear parallel polarization character with respect to the chain direction. This means that the direction of the transition dipole at 435 cm^{-1} is parallel to that of the main chains of the polyimide molecules and then the band at 435 cm^{-1} is the parallel one.

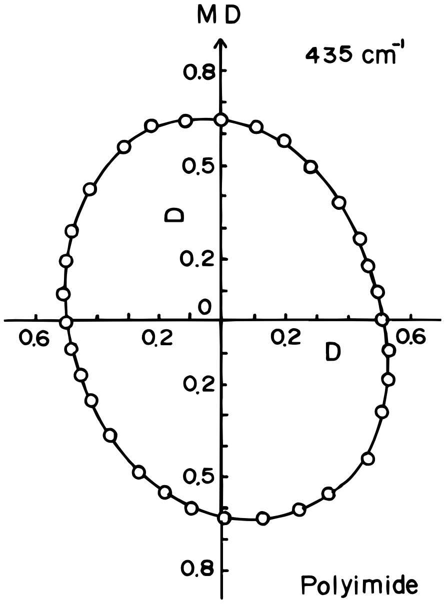


Figure 6. Angular dependence of polarized infrared absorbance D of the band at 435 cm^{-1} for the polyimide film 1-1.

On the other hand, the angular variation of the absorbance D of this band measured for the polyimide film 1-1 in question is shown in Figure 6, for which the molecular chain is considered to incline on an average by 32° from the MD, consistent with the results obtained from the dielectric data mentioned above. Thus, it was found that the direction of the maximal absorbance at 435 cm^{-1} in the polyimide film was consistent with that for ϵ' and ϵ''. The fact suggests that the main chains of polyimide molecules are preferentially aligned in the direction of the maximal ϵ' and ϵ'' and the β.

The angular variation of the breaking strength BS measured for the polyimide film 1-3 is shown in Figure 7: the BS is the largest at $\theta = 33°$. The corresponding anisotropic curve of the elastic modulus E also has a maximum at $\theta = 35°$. Thus, the dielectric, infrared, and mechanical data indicate consistently that the average orientation angle of polyimide chains in the film is about 34°.

In this way, all the data of microwave attenuation, complex dielectric constant, polarized infrared spectra, mechanical breaking strength, and elastic modulus are consistent with one another and give similar orientation patterns.

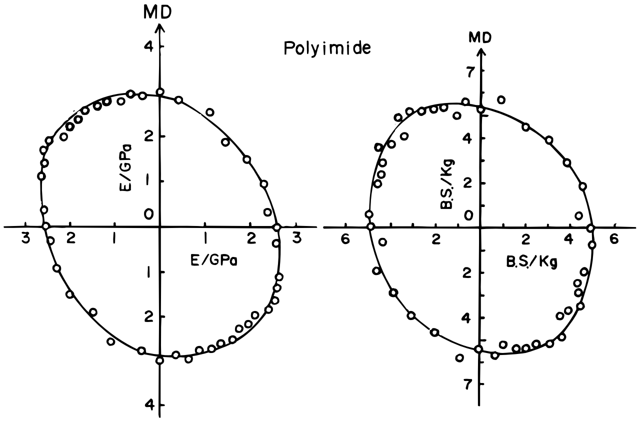


Figure 7. Angular dependences of mechanical breaking strength (BS) and elastic modulus E for the polyimide film 1-3.

Discussion

We have shown that the maximal directions of the mechanical breaking strength, elastic modulus, and infrared absorbance agree well with one another. The results showed that the molecular chains of polyimide are preferentially aligned in the direction of β. Thus we may conclude that the molecular chain of Kapton 100H film is inclined by about 35° from the MD. The maximal dielectric loss constant and dielectric loss were found also at the same rotation angle. That is to say, the largest change in dipole moment of the sample occurs in the direction of the main chain. Poly(4,4′-oxydiphenylpyromellitimide) (Kapton 100H) was speculated to take a planar zigzag conformation in both the amorphous and crystalline regions.[25,26] Therefore, the above-mentioned good correlation between the dielectric anisotropy and the chain orientation indicates that the dielectric loss of polyimide at 4.0 GHz may originate from such local motions as the twisting of the main chain oriented about 35° from the MD.

The direction (β) of minimal transmitted microwave intensity corresponds to that of the main chain of polyimide molecules. In that direction, the frequency shift may be the largest or the transmitted microwave intensity may be the smallest.[15] The direction also corresponds to that of largest ϵ' and ϵ''. This means that the orientation pattern determined by the microwave method is applicable to the determination of molecular orientation of polyimide films.

The room temperature is far below the glass transition temperature of Kapton, which is estimated to be ca. 410 °C. The polyimide film consisting mainly of the amorphous region is a good insulator at audio frequencies since $\tan \delta = \epsilon''/\epsilon'$ at 25 °C is ca. 0.004 at 10 kHz. However, the $\tan \delta$ of 0.008−0.009 at 4.0 GHz is relatively large in comparison with that at audio frequencies. This suggests an existence of relaxation at microwave frequencies, which may be ascribed to the local motion of the molecular chain of polyimide. In the frequency dependence of ϵ' and ϵ'' for Kapton 100H, the maximal value of ϵ' decreased gradually from 3.72 to 3.34 with increasing frequency from 4 to 6 GHz while the value of ϵ'' decreased rapidly from 0.035 at 4.0 GHz to 0.023 at 6.0 GHz with increasing frequency.[27] This also suggests that the ϵ'' at 4.0 GHz for polyimide films corresponds to the shoulder of dielectric relaxation and its dielectric loss peak should be observed at frequencies lower than 4.0 GHz, as shown for PET film.[13,21] Such dielectric property and its anisotropy of polyimides should be considered for use as the ultrahigh-frequency materials.

The ϵ' at 4.0 GHz of polyimide films is the sum of the dielectric increment from the dielectric relaxation due to the local motion of the chain at microwave frequencies and that from the electronic polarization due to the displacement of electron clouds around the polymer molecules at visible wavelength,[12,20] while the ϵ'' at 4.0 GHz comes from contribution of the dielectric relaxation at microwave frequencies in the crystalline and/or amorphous regions. It may be difficult to correlate simply the direction of maximal ϵ' with that of main chains of polyimide molecules because the ϵ' are based mainly on two kinds of contributions, as described above. In the present study, however, the direction of main chains in the polyimide molecules was determined from the results of the infrared dichroism as well as the case of poly(ethylene terephthalate) films.[7]

The present microwave method will give useful information for studying the molecular orientation, even for thick and colored polyimide films, and the dielectric properties at microwave frequencies, for detecting a small difference in the molecular orientation, and also for controlling the quality of the polyimide films.

It is expected that a microscopic discussion should be made from the viewpoint of the chemical structure. From such a point of view, in the near future, effects of annealing upon the microwave dielectric properties of the polyimide films will be reported.

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