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Anisotropic conductivity in stretch-oriented polymers measured with coherent microwave transient spectroscopy

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Stretch-oriented and doped polyacetylene and polyaniline are characterized using the coherent microwave transient spectroscopy technique. Conductivities parallel and perpendicular to the direction of elongation are determined. The measured orientation dependence of the sample transmissions are observed to follow the predictions of theory.

INTRODUCTION

Conducting polymers are currently of much technological interest due to several potential applications, for instance, in areas such as rechargeable batteries, electrochromic devices, and sensors.[1,2] This is predominantly a result of the development of processable and environmentally stable materials.[3,4] Moreover, the variety of rich phenomena associated with conducting polymers has resulted in an intense scientific effort to develop and study them.[5–7] An example is the extremely wide range of conductivities which have been attained with iodine-doped polyacetylene, reaching metallic values in the last few years.[1,8,9] When oriented by stretching, polyacetylene also exhibits a large anisotropy in its conductivity due to the increased mobility of electrons along the oriented polymer chains.[10–12] This property has recently been observed in polyaniline as well.[13]

In this paper, characterization of the anisotropic conducting properties of stretch-oriented and doped polyacetylene and polyaniline are presented. The measurements are carried out using the recently developed coherent microwave transient spectroscopy (COMITS) technique.[14,15] COMITS is based on picosecond duration electromagnetic transients radiated and received by optoelectronically pulsed antennas. The transients contain components over a wide range of frequencies and are useful for spectroscopy applications from 15 to 130 GHz. We begin by describing the COMITS technique and its application in the characterization of anisotropic materials. Then, results of our studies on the anisotropic electrical properties of stretch-oriented and doped polyacetylene are presented, followed by corresponding results for polyaniline. These results include the orthogonal condutivities for particular samples and the orientation dependence of their microwave transmission. The paper is then summarized.

EXPERIMENT

The COMITS experimental setup, used to make the broadband microwave measurements, is shown schematically in Fig. 1. It consists of a transmitting and a receiving antenna with the sample to be characterized located between them. The transmitter and receiver shown in Fig. 1 are photolithographically fabricated on silicon-on-sapphire substrates.[16] The photoconducive silicon epilayer is subsequently ion implanted to reduce the carrier lifetime to less than 1 ps. Optical pulses of 1.5 ps duration at 240 MHz repetition rate, obtained from a mode-locked, pulse-compressed and frequency doubled Nd:YLF laser are divided into two beams of about equal intensity. The first (pump) beam is used to excite the dc-biased transmitter. The 2.5 ps wide current pulses thus generated radiate into free space as they propagate in the transmitting antenna.[17] We use exponentially tapered coplanar stripline antennas in our experiments for several of their desirable broadband characteristics.[16] The radiated and freely propagating electromagnetic pulse induces a transient voltage at the receiver when it arrives there. This voltage is photoconductively sampled using the suitably delayed probe beam.[17] The measured signal has a 7 ps wide central peak and contains frequency components between 0 and 150 GHz.[14] Since it is proportional to the electric field (and not power) incident on the receiver, phase information is preserved. Hemispherical fused silica lenses collimate the pulsed microwave radiation diverging from the transmitter, and refocus it onto the receiver. This increases the received signal strength and facilitates greater antenna separation.[15,18] In addition, with collimated microwave radiation, the correction to account for the refraction that occurs at the sample/air interface is avoided.[15]

When a sample is inserted between the transmitter and receiver, the measured electrical signal undergoes attenuation and time delay due to the loss properties and permittivity of the material, respectively. A COMITS measurement is carried out by recording waveforms with and without the sample. The two sets of temporal data are Fourier transformed and the first spectrum is divided by the second. The result simultaneously provides both the amplitude and phase of the electric-field transmission function of the sample over a wide frequency range, typically 15–130 GHz.[14] Additional details of the experimental technique and the analysis used to extract useful material data are given elsewhere.[14–17]

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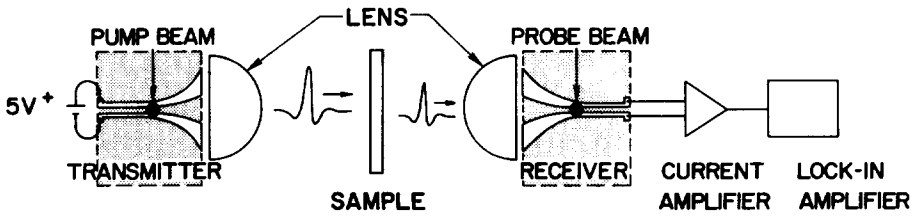

FIG. 1. Schematic of the COMITS experimental setup.

The transient electromagnetic radiation, propagating between the transmitter and receiver, is strongly polarized with the electric field parallel to the plane of the antennas. This property of the COMITS setup was used to characterize the anisotropic dielectric properties of uniaxial crystals.[19] Here we concentrate on its application in measuring the loss properties of doped polymers. While four-probe and multicontact measurement techniques have been used in the past to determine orthogonal conductivities in stretch-oriented polymers,[20] they suffer from the need for complicated calculations to extract useful material data. This follows from the fact that the sample has to be contacted at several points, and the effect of these contacts and the spreading resistance from source to sink points has to be properly accounted for. Consequently, the error bars on the resulting conductivity numbers are usually large.[20] In addition, with contact techniques, angle-dependent measurements are usually not possible.

To prepare a sample for use with COMITS technique, several 0.7 cm wide strips of the material to be characterized were mounted on a nonconducting frame made of polyimide. The strips overlap slightly to form a sample that is about 4.5 cm $\times$4.5 cm in overall dimension. Since the collimated microwave beam is about 3 cm in diameter, this size is adequate for accurate measurements.[18] The sample is inserted in the position shown in Fig. 1 and its frequency-dependent amplitude transmission function is determined as described previously. The measurement is repeated for several angles (θ) between the electric field and the direction along which the polymers are stretched. This angle will henceforth be referred to as the orientation angle. Results were obtained for values of θ between $-90°$ and $+90°$ at 15° intervals. $\theta = 0$ is the direction along which the samples were stretched and the conductivity (and transmission loss) are the highest.

THEORY

The frequency-dependent transmission of the samples was modeled using a transmission-line analog of plane-wave propagation through uniform stratified media. This is an exact and complete analogy.[21] With this procedure, the complex electric-field transmission function corresponding to either of the two principal orientations, for an anisotropic loss dielectric, is given by

$$\tilde{T}(f) = \frac{2}{2\cosh \gamma l + \{Z_1/Z_0 + Z_0/Z_1\}\sinh \gamma l}, \quad (1)$$

where

$$\gamma = \sqrt{j\omega\mu_0(\sigma + j\omega\epsilon)}, \quad (2)$$

$$Z_1 = \sqrt{\frac{j\omega\mu_0}{\sigma + j\omega\epsilon}}, \quad (3)$$

and

$$Z_0 = \sqrt{\mu_0/\epsilon_0}. \quad (4)$$

σ is the conductivity, ϵ the permittivity, and l the thickness of the sample, respectively. ω is the angular frequency ($2\pi f$, where f is the frequency). ϵ_0 and μ_0 are the vacuum permittivity and permeability, respectively. Here, Z_1 and Z_0 are the "characteristic wave impedances" of the material and vacuum.[21] The expression for $\tilde{T}(f)$ [Eq. (1)] includes the effect of the reflections at the sample–air interfaces and contains both amplitude and phase information. For samples which satisfy the conditions of $l \ll \lambda$, $l/\delta \ll 1$, and $\sigma \gg \omega\epsilon$ (where λ is the microwave wavelength and δ is the skin depth at the highest frequency), the equation for $\tilde{T}(f)$ reduces to

$$\tilde{T}(f) = \frac{1}{1 + (1/2)\sigma Z_0 l}. \quad (5)$$

This implies negligible phase retardation as was observed experimentally. Values for the conductivities of the doped polymers were obtained by fitting Eq. (5) to the experimental data. The measured transmission ($T_\parallel$) corresponding $\theta = 0°$ was used to determine the conductivity parallel to the direction of elongation ($\sigma_\parallel$) and the data corresponding to $\theta = 90°$ ($T_\perp$) was used for the perpendicular conductivity ($\sigma_\perp$). The model assumed frequency-independent material parameters in all cases. While this assumption might not be strictly valid, it was found to be a reasonable approximation for analyzing the experimental data. Additional work is required to fully clarify the conduction mechanisms in elongated and doped polymers and to develop a functional relationship between frequency and conductivity in the microwave spectrum.

By decomposing the electromagnetic radiation along the principal directions, it can be shown that the orientation-dependent transmission of stretch-oriented polymers is given by

$$T(\theta) = T_\parallel + (T_\perp - T_\parallel)\sin^2\theta, \quad (6)$$

where $T_\parallel$, $T_\perp$, and θ were defined previously.[19,22] The measured values for $T(\theta)$ were compared with the theoretically expected curves given by Eq. (6) for both materials. The higher conductivity parallel to the direction of elongation, in stretch-oriented and doped polymers, is believed to be due to the higher mobility of conduction electrons along the oriented polymer chains.[23] In fact, the analogous confinement of current flow along the wires of a wire grating result in its useful polarizing properties.[24] Indeed, Eq. (6) is also the

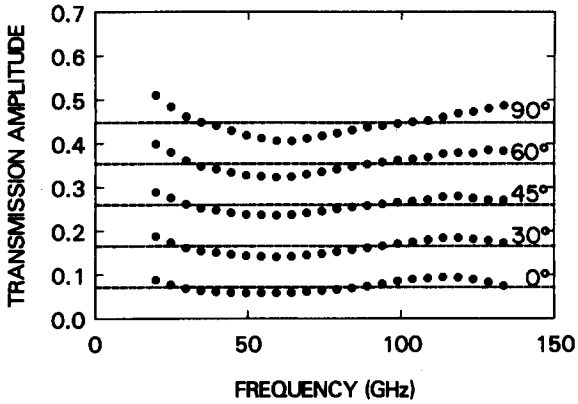

FIG. 2. Frequency-dependent electric-field amplitude transmission of stretch-oriented and doped polyacetylene, measured at various orientation angles between the electric field and the stretching direction. The dots are experimental results; the lines are results of the model.

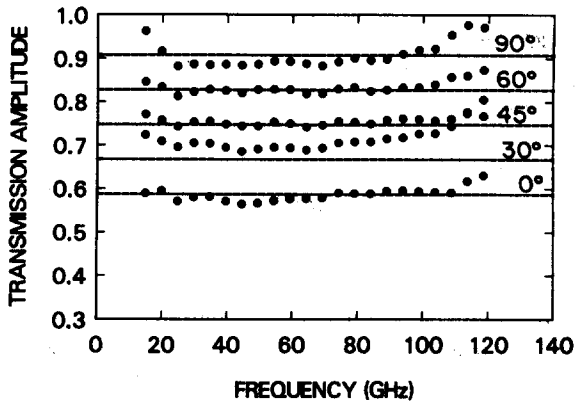

FIG. 4. Frequency-dependent electric-field amplitude transmission of stretch-oriented and doped polyaniline, measured at various orientation angles between the electric field and the stretching direction. The dots are experimental results; the lines are results of the model.

orientation dependent transmission of a polarizing element with a polarization sensitivity of $T_\perp/T_\parallel$.

POLYACETYLENE

The stretch-oriented and doped polyacetylene was prepared following a procedure described previously.[8,25] After elongation, the final material was six times as long as the starting film and 20 μm thick. A dilute I_2/CCl_4 solution (4 g/ℓ) was used for doping in order to obtain conductivities not exceeding 200 s/cm. In the usual notation $[CH(I_3)_y]_x$, the doping level of the sample used in this study corresponds to $0.01 < y < 0.015$. Indeed, with concentrated solutions of I_2 in CCl_4 (26.5 g/ℓ) maximum conductivities up to 7×10^4 s/cm have been obtained.[26]

The measured frequency-dependent electric-field transmission of the polyacetylene sample is shown in Fig. 2 for several orientation angles. The points on the figure correspond to experimental data, while the lines are results of the simulation discussed in the theory section. From the best fit between theory and experiment, the parallel and perpendicular conductivities are determined to be $\sigma_\parallel = 34.4 \pm 8.0$ s/cm, and $\sigma_\perp = 3.3 \pm 0.6$ s/cm, respectively. The main contribution to the error margin comes from the scatter in the experimental points. The experimentally measured values of $T(\theta)$ at 60 GHz are plotted in Fig. 3 together with the theoretically expected curve given by Eq. (6). Values of $T_\parallel = 0.06$ and $T_\perp = 0.41$ were used in the calculation. The agreement between experiment and theory is excellent. We have observed conductivity ratios of up to 15 in other polyacetylene samples.

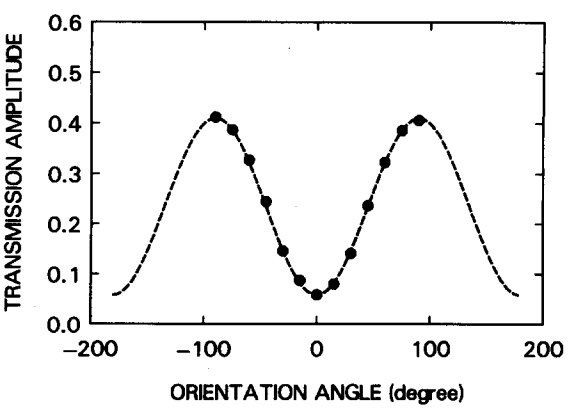

FIG. 3. Amplitude transmission of the polyacetylene sample, at 60 GHz, plotted as a function of orientation angle. The dots are experimental results; the dashed line is calculated from Eq. (6), with $T_\parallel = 0.06$, and $T_\perp = 0.410$.

POLYANILINE

The polyaniline sample discussed in this paper was synthesized with the technique described in Ref. 13. The stretch alignment was performed as follows: A polymeric stretchable support such as polypropylene was clamped in a laboratory stretching device and a 5% solution of polyaniline (emeraldine base) in *N*-methyl pyrrolidinone (NMP) was poured over it. An infrared heating lamp (250 W) was placed ~20 cm away and the solvent was evaporated at 20 °C until the semisolid mixture was "tacky" to the touch. Then the temperature was raised to 100 °C and the stretching was commenced at a rate of ~1 cm/min. The stretching was continued until the length of the sample was ~five times the original length. The elongated films were doped with 1 M solutions of HCl for 12 h and washed in distilled water, methanol, and diethyl ether. The sample was then placed under a vacuum for 10 h. With high levels of doping, conductivities of up to 240 s/cm were measured in the direction of elongation for this new polyaniline material.[26]

The frequency-dependent transmission for the polyaniline sample is shown in Fig. 4 together with results of the simulation discussed in the theory section for several orientation angles θ. As before, the orthogonal conductivities are determined, from the best fit between experiment and theory, to be $\sigma_\parallel = 1.93 \pm 0.12$ s/cm, and $\sigma_\perp = 0.28 \pm 0.06$ s/cm, respectively. The measured amplitude transmission at 60 GHz is plotted as a function of the orientation angle in Fig. 5, together with the theoretical curve given by Eq. (6). Values of $T_\parallel = 0.58$ and $T_\perp = 0.89$ were used in the calculation. The agreement between experiment and theory, though not as close as for the polyacetylene sample, is still quite

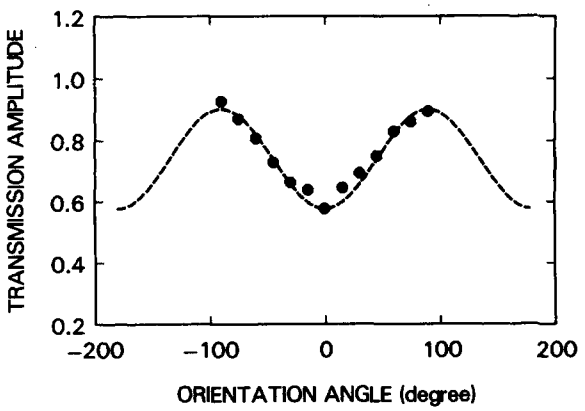

FIG. 5. Amplitude transmission of the polyaniline sample, at 60 GHz, plotted as a function of orientation angle. The dots are experimental results; the dashed line is calculated Eq. (6), with $T_{\parallel} = 0.58$, and $T_{\perp} = 0.89$.

good. The individual strips which make up the polyaniline sample did not overlap as closely as would be desired due to some wrinkling at the edges. This could be responsible for the discrepancies observed in Fig. 5.

SUMMARY

In summary, the recently developed coherent microwave transient spectroscopy technique was used to characterize the anisotropic conducting properties of stretch-oriented and doped polyacetylene and polyaniline. Electrical conductivity parallel and perpendicular to the direction of elongation were determined. The orientation-dependent microwave transmission of these samples is in good agreement with predictions of theory. The large differences in orthogonal conductivities is due to the predominant conduction of electrons along the oriented polymer chains. This feature of stretch-oriented polymers could make them useful as microwave polarizers. Indeed, a common optical polarizer, the Polaroid *H* sheet, is a stretch-oriented and doped polyvinyl alcohol.[27]

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