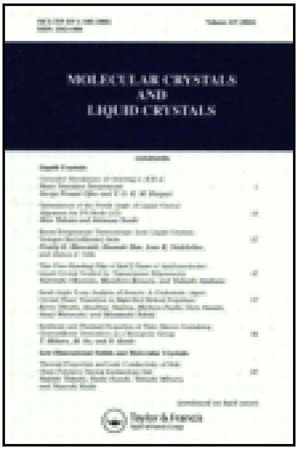

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Dielectric Properties of Polypyrrole Doped with Tosylate Anion in the Far Infrared

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Dielectric Properties of Polypyrrole Doped with Tosylate Anion in the Far Infrared

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The dielectric constants and optical conductivities of films of conducting polypyrrole with different doping levels were investigated. Measurements were carried out in the far infrared region (10–200 cm^{-1}) and dielectric properties were determined by analysis of reflection and transmission intensities at normal incidence. The samples were prepared electrochemically, providing control of the doping level through reduction of the as grown (oxidized) film.[1] Electrical conductivity measurements were performed with a four-point probe. A method to determine the real and imaginary parts of the complex index of refraction is described. The magnitude and dispersive nature of the complex index of refraction is described for a number of samples with different levels of conductivity. It is shown that the dependence of the dielectric constants of conducting polymers on conductivity and the ability to manipulate this parameter through the doping process present significant possibilities in controlling the dielectric properties of materials.

INTRODUCTION

The dielectric behavior of conducting polymer materials has been investigated only in recent years with little attention paid to the very low frequency (less than 100 cm^{-1}) region of the spectrum.[2] In this study the dielectric constants and optical conductivities of differently prepared films of conducting polypyrrole were determined at frequencies in the far infrared (FIR) by analysis of reflection and transmission intensities at normal incidence. The free standing films are noted for their good mechanical properties and stable conductivity at room temperature.[3] The heavily doped films exhibit large real and imaginary parts of the complex index of refraction (n-ik) and are highly dispersive at these frequencies. Moreover, the conductivity and the real and imaginary parts of the index of refraction n-ik, can be varied two or three orders of magnitude in a controlled way through the processes of oxidation and reduction. The dispersive nature of the complex index of refraction at low frequencies is quite remarkable and likewise can be tailored during the growth process. The dependence of the dielectric constants of conducting polymers on conductivity and the ability to manipulate this parameter in the electrochemical process present significant possibilities in controlling the dielectric properties of materials. It is expected that characterization of the dielectric constants of the doped polymers at low frequencies will be useful in determining the method of conduction in these materials as a function of the polymer microstructure. It has been our intention to characterize the dielectric functions of these materials and thus improve the knowledge of them sufficiently for application in the fabrication of devices, as well as to provide some information supporting the theoretical understanding of conducting polymers.

SAMPLE PREPARATION

Conducting polymers such as polypyrrole may be simultaneously polymerized and doped at the working electrode of an electrochemical cell. The use of appropriate electrolyte provides the dopant counter ion. This approach leads to the growth of uniform thin films covering the entire working electrode. This is the method of choice when films with controlled thickness and tailored electrical properties are desired. The nature of dopant and level of doping can be exactly controlled by controlling the current passed through the electrochemical cell. In addition, the film grows in intimate contact with the electrode and conforms to its shape. For dielectric measurements in the FIR regions, large area, smooth and flat films are essential.

Free standing films of polypyrrole doped with tosylate anion are synthesized by using a platinum foil as the working electrode in an acetonitrile solution containing 0.1 M pyrrole and 0.25 M tetraethylammonium tosylate. A carbon plate serves as the counter electrode and a calomel reference electrode is used to monitor the working electrode potential during the galvanostatic synthetic process. By passing a current of 0.4 mA/cm^2 for a period of 4 hrs, oxidation and polymerization occur simultaneously, producing a black conducting film several microns thick at the electrode. The film is immersed in acetonitrile for 15 minutes and dried under vacuum at room temperature.[1]

DATA ANALYSIS

Measurements of reflection and transmission intensities were performed in the far infrared (FIR) utilizing an FTIR (Fourier transform infrared) spectrometer. A Michelson interferometer modified to include an enlarged sample compartment was used to carry out the measurements. Measurements of reflection and transmission are performed at normal incidence with an accuracy of 5 percent. As prepared, the polymer films were typically six square centimeters. The optical beam is apertured down to expose approximately 2 cm^2 of the sample. In the reflection measurement, the collimated output of the interferometer is collected, focused on the sample, and recollected in an approximate f/5 optics system consisting of two off axis parabolic mirrors, a flat gold mirror and a TPX lens. The sample holder as well as the background mirror is mounted on a translation stage allowing for consecutive measurements of sample and background without breaking vacuum. In the transmission mode, the sample is mounted near the output aperture of the sample box and the radiation focused down to a spot size of approximately two centimeters.

A Mercury lamp source combined with mylar beam splitters of different thicknesses provides black body radiation in the spectral region between 10 and 200 cm^{-1}. The radiation power in the FIR is only a few nanowatts, and the transmittance of the polymer films may be less than 0.01 percent. A silicon bolometer cooled to 1.8 K with a sensitivity of 3×10^{-14} $Watts/Hz^{1/2}$ is employed for this reason. The entire system is operated under vacuum to reduce the signal loss associated with water absorption in the FIR.

To further enhance the reliability of the R and T data, additional measurements are performed with high power (10 mW) HCOOH lasers at discrete frequencies for comparison with the FTIR data. The laser sources also extend data acquisition to frequencies below 8 cm^{-1}.

Determination of the real and imaginary parts of the complex index of refraction is accomplished by application of the Fresnel equations to measurements of R and T at normal incidence. The complex reflection and transmission amplitudes are given below:

$$r = \rho(1 - e^{i\beta})/(1 - \rho^2 e^{i\beta}) \tag{1}$$

$$t = (1 - \rho^2)e^{i\beta/2}/(1 - \rho^2 e^{i\beta}) \tag{2}$$

with

$$\rho = (1 - n_c)(1 + n_c)$$

and

$$\beta = 4\pi n_c d/\lambda$$

where n_c is the complex index of refraction given by $n_c = n - ik$

Although it is frequently difficult to measure transmission in materials that are highly reflecting or absorbing, the use of sensitive detectors permits the direct determination of the complex index of refraction using the Fresnel equations. This is more convenient than the Kramers-Kronig method and especially useful when collecting data over a narrow frequency range. The Kramers-Kronig method depends on very accurate reflection measurements taken over a broad frequency range and extrapolation of data to estimate R_0 and $R\infty$.

The Fresnel equations in exact form are multiple valued functions of R and T. The transcendental nature of the equations requires a computerized numerical technique for their solution. We have developed software similar to that described by Nestell and Christy[4] in which one plots the constant contours of R and T in a plot of n vs k. The intersections of R and T give all the possible paired values of n and k satisfying the Fresnel equations and can be determined by a numerical root searching routine. As an example of this technique, in Figure 1 the contours of constant reflection and transmission with R = 0.167 and T = 0.774 are plotted

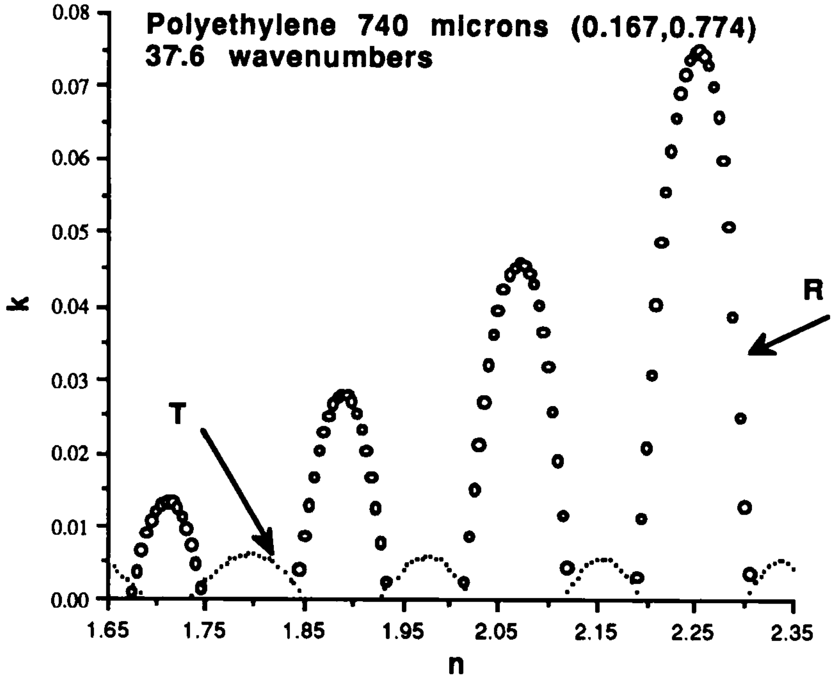

FIGURE 1 Contours of constant R and T.

for a 737 micron thick Polyethylene film. Some of the possible solutions are given below in Table 1.

The selection of the physically correct root from among the possibilities indicated in this manner typically requires performing additional measurements and can be accomplished in several ways. For example, n and k derived from samples of different thicknesses will provide a common pair of physical roots.

RESULTS AND DISCUSSION

Figures 2 and 3 are plots of the complex index of refraction for fully oxidized films with measured dc conductivities in the 40–100 mho/cm range. The large dispersion of n and k is apparent in the doped (as grown) films. Reducing the polypyrrole films produces large variations in the measured levels of dc conductivity as well as the dielectric constants. The data indicates that the dielectric constants are highly dispersive in the heavily doped films. The values of n and k can be varied over a broad range by controlling the level of doping. In Figure 4 the optical conductivity is plotted as a function of doping for films ranging between heavily doped and reduced 1 hour in which the conductivity of Polypyrrole is seen to vary over three orders of magnitude.

TABLE I

Multiple root pairs for Polyethylene at 37 cm^{-1}

real n	imaginary k
1.675	.0008
1.730	.0017
1.830	.0040
1.930	.0027

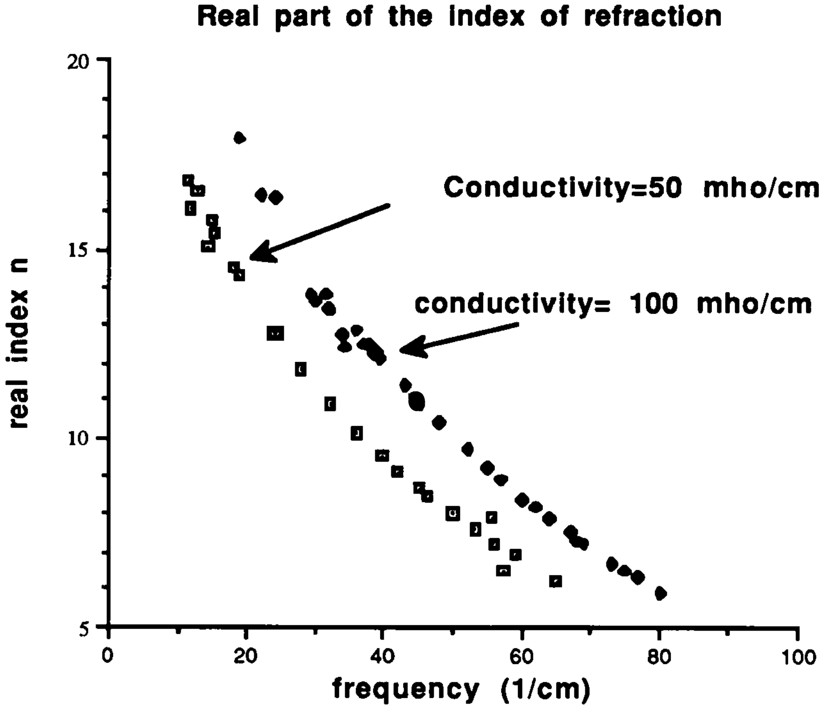

FIGURE 2 Plot of the real part of the refractive index against wavenumber in the FIR region for two conducting polypyrrole films with dc conductivity as shown.

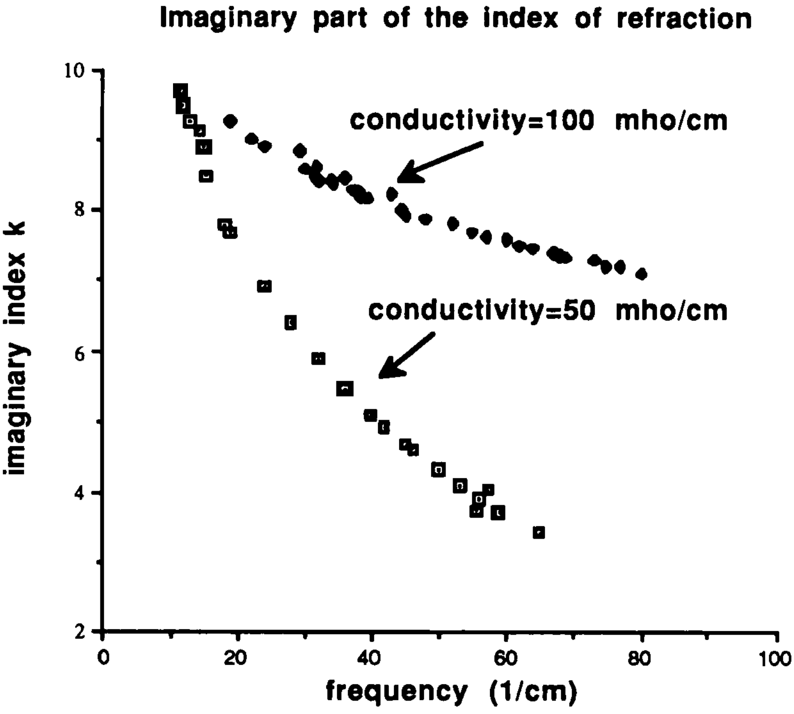

FIGURE 3 Plot of the imaginary part of the refractive index against wavenumber in the FIR for two conductive polypyrrole films with dc conductivities of 50 and 100 mho/cm.

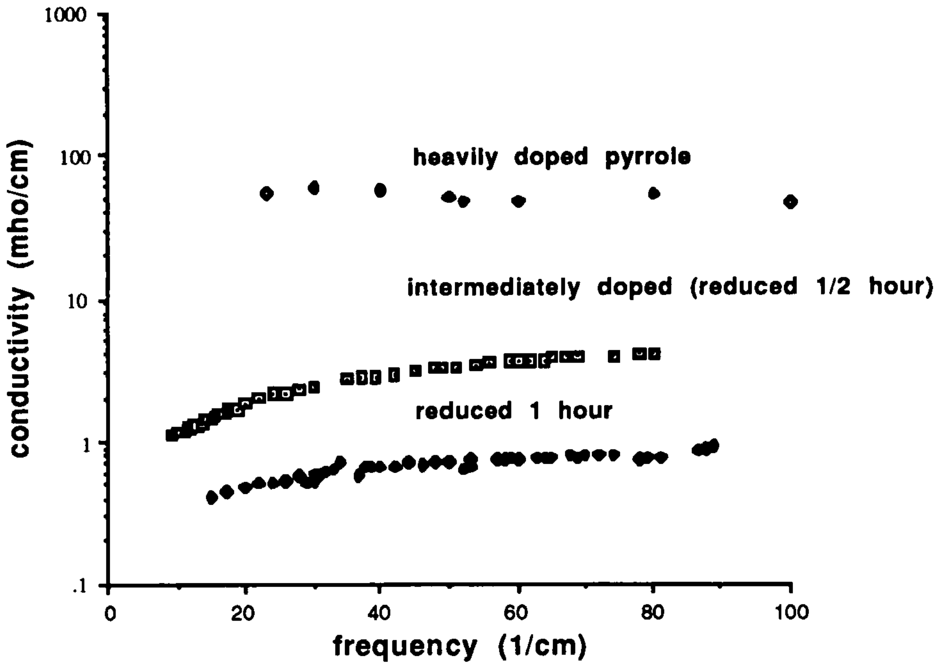

FIGURE 4 Optical conductivity of polypyrrole films fully oxidized and subsequently reduced to different levels of oxidation.

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