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High-frequency dielectric response of polyaniline pellets as nanocomposites of metallic emeraldine salt and dielectric base

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ABSTRACT

Conducting polyaniline (PANI) salt and dielectric PANI base pellets were studied in the infrared (IR) and terahertz (THz) range at room temperature and compared with the IR transmission spectra of powdered samples dispersed in potassium bromide and with those of thin films. The IR reflectivity combined with THz transmission was fitted to calculate the permittivity and IR conductivity spectra. In addition to vibration modes and Drude contribution of the free carriers in the conducting PANI, strong and broad mid-IR absorption was detected and assigned to localized carriers. Additional absorption in the far IR, much stronger in case of the conducting PANI, was assigned to Boson peak. Good agreement between the IR conductivity peaks and those from the absorbance evaluated from the transmission measurements was obtained and differences between the spectra of PANI salt and base are discussed. The dielectric and conductivity spectra of PANI salt were modeled as the spectra of a composite of PANI base and metallic PANI reported by Lee et al., Nature **441**, 65 (2006). Effective medium approach using three different models was applied and discussed. The best results, including the semiconductor-like temperature dependence of the low-frequency conductivity, were obtained with the generalized Lichtenecker model. The strong permittivity increase on decreasing frequency below the THz range is discussed and compared with the literature data.

1. Introduction

Polyaniline (PANI) is the best-studied classical conducting polymer. Its DC conductivity can be influenced by processing, level of protonation or oxidation, and mesoscopic order from $\sigma_{DC} \approx 10^{-12}$ S cm^{-1} (PANI base) up to $\approx 10^{3}$ S cm^{-1} (PANI salt), i.e., from a typical dielectric up to the metallic behavior, as reviewed in several excellent papers [1–7]. The conduction mechanism consists of polaron transfer along the polymer chains and also their tunneling across the chains particularly in the ordered (crystalline) nanoregions. Since, as a rule, the PANI salt samples are not fully ordered, the conductivity even for the conducting emeraldine salt can vary between ≈ 1 and 10^{3} S cm^{-1} and usually shows a semiconductor behavior of the temperature dependences. There is one exception, not mentioned in the recent reviews [4–7]. In 2006, Lee et al. [8] succeeded to prepare PANI films by using polymerization in a self-stabilized dispersion described in [9], with the room-temperature DC conductivity as high as ≈ 1200 S cm^{-1}, which monotonically increased on cooling (about two times down to 5 K). The IR reflectivity data up to 2000 cm^{-1} of the best conducting films have been well fitted with a simple Drude model including the DC conductivity data. This behavior, together with temperature dependence of the DC conductivity, is in full agreement with simple metallic behavior. The other conductivity extreme, the deprotonated form (PANI base), is an amorphous dielectric.

Recently, we have carried out broadband dielectric measurements (10^{-2}–10^{13} Hz) including temperature dependences down to 10 K of three types of PANI pellets: conducting, semiconducting and non-conducting PANI base [10]. Here we study two of them in more detail at room temperature: the conducting PANI emeraldine salt (PS, $\sigma_{DC} \approx 1$ S cm^{-1}) and the non-conducting PANI emeraldine base (PB, $\sigma_{DC} \approx 10^{-12}$ S cm^{-1}), obtained by deprotonation of the emeraldine salt. As it is generally believed that the differences in the conductivity of PANI salts are mainly due to various degrees and types of disorder, which prevent conduction of polarons on macroscopic distances, we have decided to model the complex dielectric and conductivity response of our samples as nanocomposites of the metallic PANI (PM) response [8] and that of dielectric PB. Since our broadband dielectric spectroscopy includes also the IR range, we compare in detail the IR conductivity spectra

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obtained from fitting the IR reflectivity with the standard absorbance spectra obtained from IR transmission measurements on powdered PANI in potassium bromide (KBr) pellets and thin PANI films.

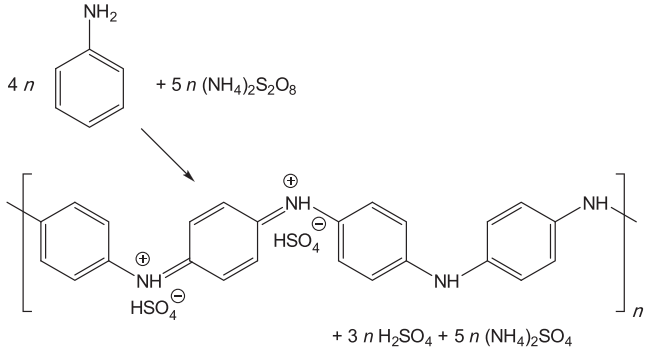
For modeling of nanocomposites we assume that both components do not interact so that their bulk AC conductivity and dielectric responses can be used as those of the pure constituents. For simulation of the complex topology of both constituents we apply the effective medium approach (EMA), which assumes sharp boundaries among the uniform nano-regions of the composite (generally of arbitrary shape) and a uniform external probing electric field within the regions of all individual components. The latter condition is expected to be well satisfied in PANI nanocomposites at least up to the IR region, since the wavelengths are still much longer than the size of individual nano-regions. To simulate the topology of the composite with a partial percolation of both components, we apply the frequently used Bruggeman EMA model [11], the generalized Lichtenecker model [12], which has been recently shown to yield very good results for the treatment of effective dielectric responses of materials with porosity of complex topology [10,13,14], and the novel single geometrical resonance (SGR) model used recently for discussion of the THz spectra of semiconductor nanoparticles [15–17].

2. Experiment and evaluation of data

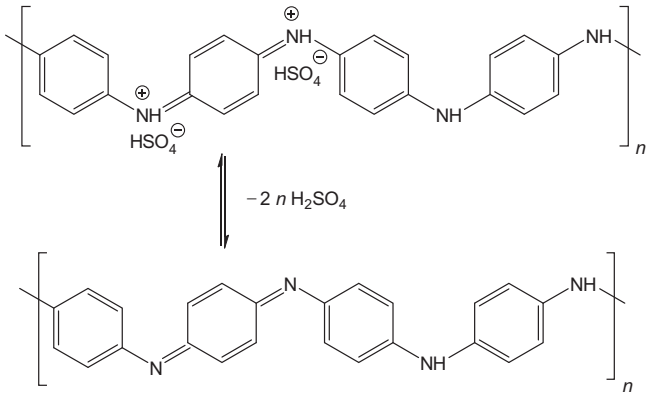
The powdered PANI salt (PS) was prepared by oxidation of 0.2 M aniline hydrochloride with 0.5 M ammonium peroxydisulfate [18] in aqueous solution at room temperature (Scheme 1).

The non-conducting PANI base (PB) was prepared by immersion of PANI salt to a 1 M solution of ammonia for 24 h (Scheme 2).

Powdered samples were compressed into pellets at 700 MPa for 5 min and their DC conductivity was determined by the van der Pauw method using SMU Keithley 237 as the current source and a Multimeter Keithley 2010. A two-point method using a Keithley 6517 electrometer was applied to samples having a low conductivity, $<10^{-5}$ S cm^{-1}. The measured DC conductivity of PS (density 1.32 g cm^{-3}) was $\sim$3 S cm^{-1} and of PB (density 1.24 g cm^{-3}) was $\sim10^{-12}$ S cm^{-1}. Selected thicker pellets with well flat surfaces were used for the IR reflectivity measurements and thinner ones (0.2 mm and 1 mm thick for PS and PB, respectively) for the THz transmission spectroscopy. The IR reflectivity spectra in the 30–3000 cm^{-1} range were measured under near-normal incidence at room temperature using Fourier transform IR (FTIR) spectrometer Bruker IFS 113v equipped with pyroelectric deuterated triglycine sulfate (DTGS) detector. In the THz range (0.2–2 THz), the complex dielectric response was obtained using the time-domain THz transmission spectrometer based on a Ti:sapphire femtosecond laser [19]. For



Scheme 1. The oxidation of aniline with ammonium peroxydisulfate yields PANI hydrogen sulfate (or sulfate). Sulfuric acid and ammonium sulfate are by-products. In the present case of the oxidation of aniline hydrochloride, besides the hydrogen sulfate anions, chloride anions contribute to the counter-ions of PANI.



Scheme 2. Deprotonation of PS, e.g., with ammonium hydroxide, to PB. Ammonium salt is produced from the acid which had protonated the PANI.

generation of the THz pulses, an interdigitated photoconducting GaAs switch was used. To detect the transmitted THz pulses, a plate of the (1 1 0) ZnTe crystal was used for the electro-optic sampling.

The normal IR reflectivity spectra $R(\omega)$ of flat opaque samples are related to the complex dielectric permittivity $\varepsilon(\omega)$ of the material:

$$R(\omega) = \left|\frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1}\right|^2 \tag{1}$$

To obtain the complex dielectric function from the IR reflectivity, we have used standard fitting procedure. For fitting the IR reflectivity spectrum of PB pellet along with the THz data we have used the generalized oscillator model with the factorized form of the complex permittivity

$$\varepsilon_{PB}(\omega) = \varepsilon_\infty \prod_j \frac{\omega_{LOj}^2 - \omega^2 + i\omega\gamma_{LOj}}{\omega_{TOj}^2 - \omega^2 + i\omega\gamma_{TOj}} \tag{2}$$

where ω_{TOj} and ω_{LOj} is the transverse and longitudinal frequency of the j-th polar phonon, respectively, and γ_{TOj} and γ_{LOj} their corresponding damping constants. The high-frequency permittivity ε_∞ results from electronic absorption processes in the visible and UV range. For fitting the IR reflectivity of the conducting PS pellet we have added the classical Drude term to the factorized permittivity (2) [20]:

$$\varepsilon_{PS}(\omega) = \varepsilon_\infty \prod_j \frac{\omega_{LOj}^2 - \omega^2 + i\omega\gamma_{LOj}}{\omega_{TOj}^2 - \omega^2 + i\omega\gamma_{TOj}} - \frac{\sigma_{DC}}{\varepsilon_0\omega(i - \omega\tau)} \tag{3}$$

where σ_{DC} is the DC conductivity, ε_0 is the permittivity of free space and $\tau = 1/\Gamma$ is the scattering (life) time of the free carriers. Real part of the IR conductivity $\sigma(\omega)$ was calculated from the imaginary part of the complex dielectric response $\varepsilon''(\omega)$:

$$\sigma(\omega) = \varepsilon_0\omega\varepsilon''(\omega). \tag{4}$$

It is well known [21] that the conductivity spectrum $\sigma(\omega)$ is the most suitable spectrum for extracting the vibrational mode parameters. For well-separated modes described by classical damped harmonic oscillator model, the conductivity peak frequencies correspond to mode frequencies (independent of damping even in the case of overdamping), the peak full widths at half maximum correspond to the mode dampings and the areas under the peaks (in the linear frequency scale) correspond to the mode (oscillator) strengths. The well-known oscillator sum rule states that the total area under the conductivity spectrum is given by all charges, which take part in the absorption process, and therefore must be finite and essentially temperature independent for a given material.