

Optical and Electrical Properties of a New Polymer

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ABSTRACT: Thin film of poly(5-isopropylidene-cyclo-1,4-vinylene-2,3-dicarboxylic acidamide-*s*-methyl hydrazinecarbodithioate) (II) (Scheme 1) of 5 μm thickness was prepared. The dielectric properties of the prepared sample were studied as a function of frequency and temperature, and the results were analyzed by the Cole–Cole method. The optical permittivity and the dc-conductivity have been deduced, and the activation energy has been calculated and found to be 0.023 eV. Also, a detailed study of optical absorption is presented. The optical absorption spectra were measured in the wavelength range from 200–600 nm. The calculated absorption coefficient, absorption index, and determined values of energy gaps (E_{opt}^d , E_{opt}^i and ΔE) are presented. The results indicate that both mechanisms of direct and indirect transitions exist. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1653–1657, 1997

INTRODUCTION

Polymers have a wide range of important applications, such as optical switching, thermochromic applications, and pyroelectricity.^{1,2} The ring-opening metathesis polymerization (ROMP) of many functionalized monomers using either homo or heterogeneous catalyst has been the subject of many studies.^{3–6} There has been increasing interest in synthesizing new polymers that possess high thermal stability and good mechanical properties. The study of absorption of exo-7-isopropylidenebicyclo[2,2,1]hepta-2-ene-5,6-dicarboxylic acidamide-*s*-methyl hydrazine carbodithioate (Scheme 1) provides a deeper understanding of the interaction processes between optical excitation (i.e., electronic excitations) and phonon spectra. The measurements of the absorption give an opportunity to obtain information about the nature of the chemical bonds between lattice units and alternations. Dielectric analysis

measures two fundamental electrical characteristics of material, namely, capacitance and conductance, as a function of temperature and frequency. These properties have more significance when they are correlated to changes in the molecular and/or structural state of the material. The actual parameters monitored using dielectric analysis are the permittivity, which is a measure of alignment of the molecular dipoles in a material; and the loss factor, which represents the energy required to align the dipoles or to move trace ions. The aim of the present work is to study the optical and alternating current (ac) conductivity of polymer (II).

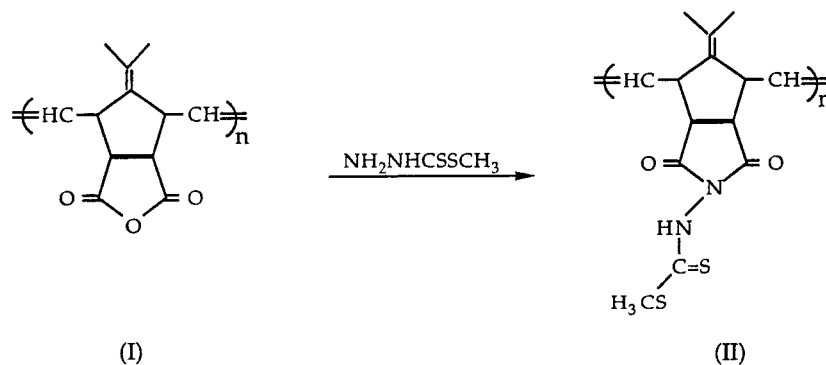
EXPERIMENTAL

Sample Preparation

Polymer (II) was prepared as shown in Scheme 1 via the reaction of *s*-methyl hydrazinecarbodithioate (0.1 mol) and the anhydride polymer (I) (0.1 mol) in dimethylformamide (60 mL). The color of the reactants changed when the required amount

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Scheme 1

of hydrazine was injected into the polymer solution. The reaction was left at 75°C overnight to allow evaporation of solvent; the polymer was collected and dissolved in acetone to give a viscous solution; it was precipitated in chloroform (150 mL), filtered, and evacuated for 24 h to yield 90%. The isolated polymer was characterized using elemental infrared (IR), and nuclear magnetic resonance H^1 (NMR) analysis.⁷

UV Measurements

The absorption measurements for polymer (II) film of 5×10^{-4} cm thickness were made using a UV-160 Shimadzu spectrophotometer in the

wavelength range of 200–500 nm. The optical density (absorbance) was directly measured from the instrument.

Dielectric Measurements

The measurements were performed in the frequency range of 0.1–100 KHz using a Hioki 3520 LCR tester operated at 0.8 V. The sample was coated with silver using an Edwards coating unit Model 306 and placed between the two electrodes of the sample holder. The impedance z and the phase angle θ were read directly from the impedance meter; hence, the real and imaginary part

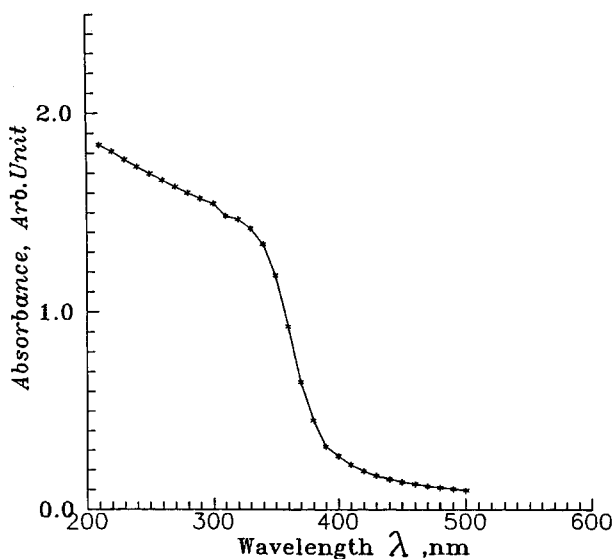


Figure 1 Optical absorption spectral distribution for polymer (II).

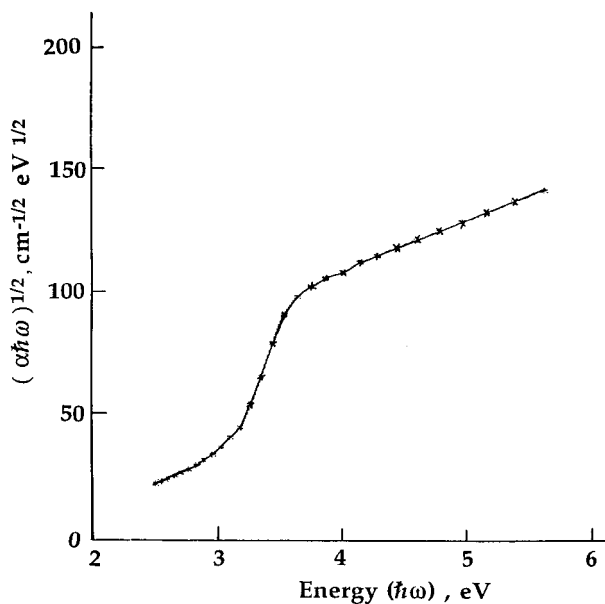


Figure 2 Variation of $(\alpha\hbar\omega)^{1/2}$ on the photon energy $(\hbar\omega)$.

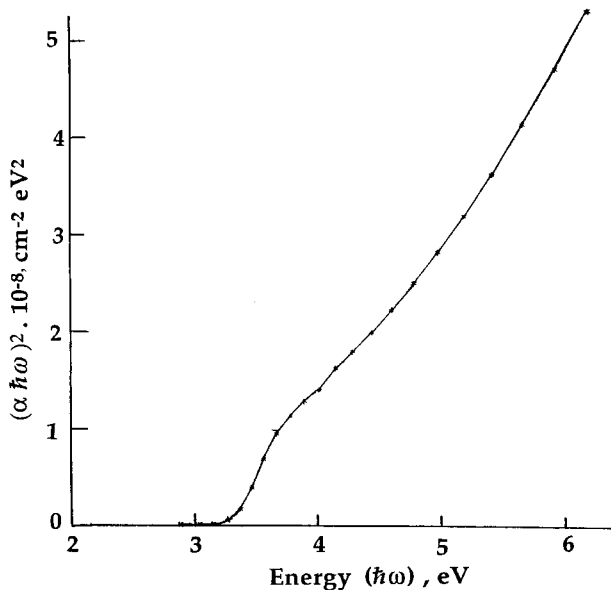


Figure 3 Dependence of $(\alpha\hbar\omega)^2$ on the photon energy $(\hbar\omega)$.

of the impedance (z' , z'') can be obtained. The capacitance c and the loss factor $\tan \delta$ were also measured in order to estimate the dielectric dispersion of the material.

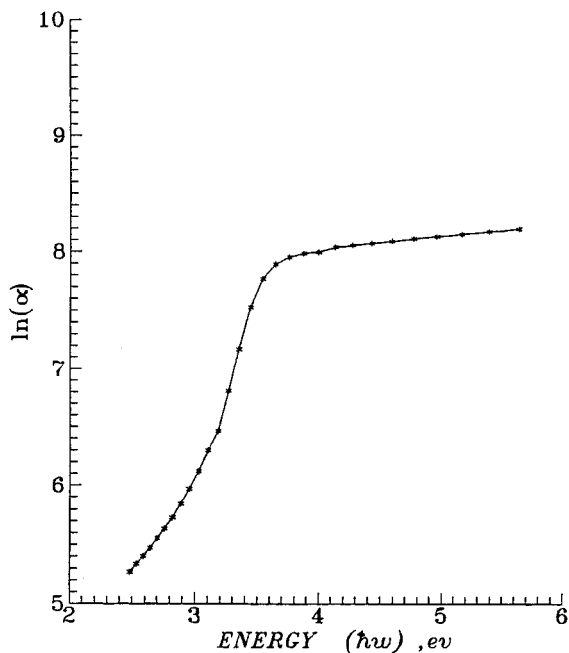


Figure 4 Variation of the absorption coefficient as $\ln \alpha$ versus photon energy.

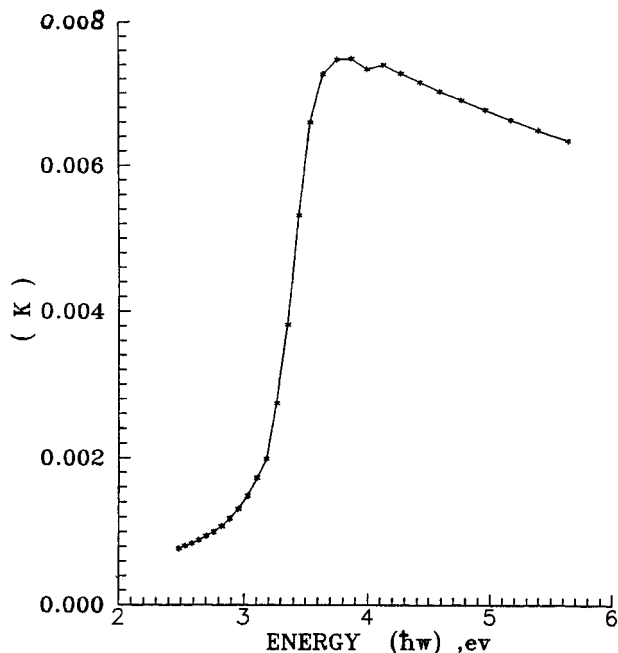


Figure 5 Spectral distribution of absorption index (K).

RESULTS AND DISCUSSION

The optical absorption spectra of the studied polymer film in the visible and UV range is shown in Figure 1. It is clear that a sharp absorption edge appears at the wavelength of 395 nm and used to study the mechanism of optical transition in polymer (II) film. The adsorption coefficient α is calculated from the optical absorbance and thickness of sample versus photon energy $\hbar\omega$. It is observed that two distinct linear relations are found to exist corresponding to different interband absorption processes. The spectral variation in α , as follows, is described by⁸:

$$\alpha\hbar\omega = \beta(\hbar\omega - E_g)^n \tag{1}$$

where β is a parameter that depends on the transition probability and E_g is the energy of transition. The lower energy range $n = 2$ is a typical of an indirect allowed transition. However, the value of $n = 0.5$ is believed to be appropriate for the higher energy absorption where direct transition occurs. The indirect optical energy gap E_{opt}^i can be obtained from the plot of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ (Fig. 2), while the direct energy gap E_{opt} can be obtained from the plot of $(\alpha\hbar\omega)^2$ vs. $\hbar\omega$ (Fig. 3); their values were found to be 2.86 and 3.26 eV, respectively. Figure 4

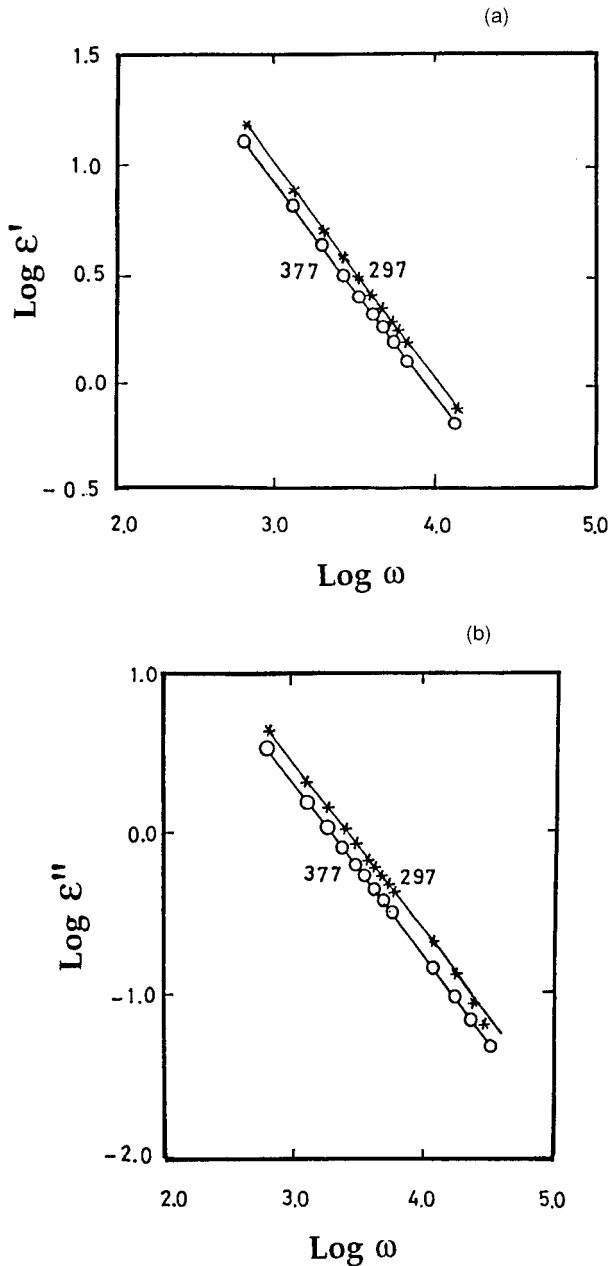


Figure 6 (a) The frequency dependence of real part of permittivity at temperatures 297 and 377 K. (b) The frequency dependence of imaginary part of permittivity at temperatures 297 and 377 K.

shows the variation of $\ln \alpha$ with photon energy $\hbar\omega$ for the studied polymer. The width of the band tail can be evaluated in the energy below 3.5 eV from the following relation:

$$\ln \alpha = \ln \alpha_0 - \hbar\omega / \Delta E \quad (2)$$

At high photon energies ($E_{ph} > 4$ eV), $\ln \alpha$ tends

to be nearly flat. The spectral distribution of the absorption index K is shown in Figure 5, and a distinct dependence of absorption index on photon energy is observed. This dependence exhibits a peak around 3.8 eV.

Electrical Properties

The dielectric functions in the time domain $f(t)$ and in the complex frequency domain $X(\omega)$ represent the most basic form of information about the dielectric properties of substance and are related to each other by a Fourier transform. The real part of the dielectric susceptibility $X'(\omega)$ is almost independent of the frequency outside the region of significant loss, remaining constant below the loss region and rapidly decreasing to zero above it. The dielectric permittivity is related to $X(\omega)$ by the following relation:

$$\epsilon(\omega) = \epsilon_0(1 + x'(\omega)) \quad (3)$$

The real and imaginary parts of permittivity as a function of frequency at different temperatures are shown in Figure 6. It is clear from this figure that the frequency response is roughly constant at high frequency and follows the dielectric response Kramers–Kronig relation.^{9,10} The low-frequency dielectric response (0.1–10 KHz) is expected from any localized charge carriers that may be present in the material, especially in the condition where the effects of the free charge carriers may contribute to dielectric relaxation in two fundamental ways which effect the delay response between current and voltage. On the other hand, these carriers may suffer a delay release from the localized

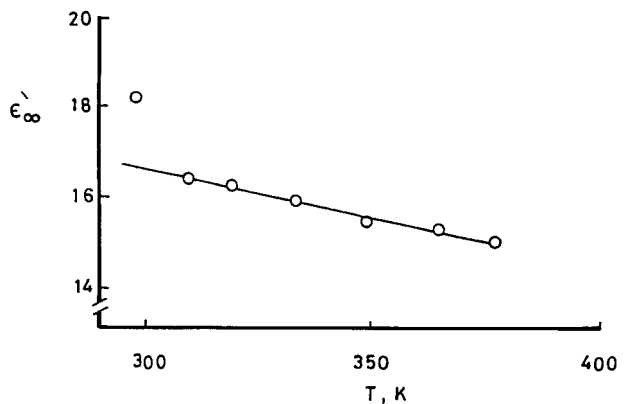


Figure 7 Variation of the optical permittivity ϵ_∞ with temperature for polymer (II).

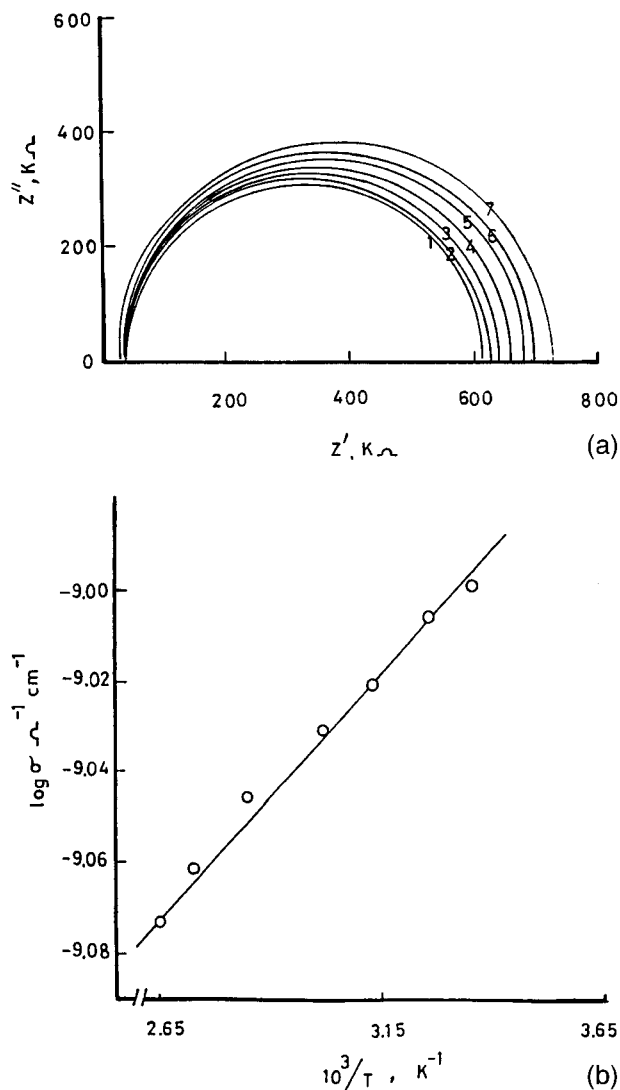


Figure 8 (a) Cole-Cole diagram of impedance at the following temperatures: 1) 297, 2) 310, 3) 320, 4) 335, 5) 350, 6) 377, and 7) 397 K. (b) Temperature dependence of dc conductivity of polymer (II).

level into the free band where they take part in the ordinary conduction process; this is a generation-recombination process. Figure 7 shows the variation of the optical permittivity ϵ'' with temperature: it is clear from this figure that ϵ'' decreases with temperature; this can be attributed to inhomogeneity and less crystalline polymer, which leads to a less ordered material. Since the

studied polymer is a polycrystalline inhomogeneous material, we can interpolate the bulk conductivity of the material involving a combination of single resistance R_{gb} (grain bulk resistance) in series with a parallel Rc circuit representing the grain boundary layer. Figure 8(a) shows the complex impedance at different temperatures, and the semicircular appearance confirms the assumption of a negligible contact impedance. The direct current (dc) conductivity in this case is governed by grain boundary resistance; on the other hand, as the temperature increases, the grain boundary resistance increases, leading to incomplete semicircles with a high grain boundary resistance. The dc conductivity as a function of temperature is written as follows:

$$\sigma = \sigma_0 \exp(-E/KT) \quad (4)$$

where E is the barrier activation energy for the jumping ion vacancies, and σ_0 is constant. From the geometrical shape of the sample and the obtained resistance, the dc conductivity at different temperatures is illustrated as shown in Figure 8(b). The slope of the straight portion in this figure gives the activation energy and is found to be 0.023 eV.

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