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Refractive index dispersion and analysis of the optical constants of an ionomer thin film

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The basic optical properties and optical constants of the ionomer thin film have been investigated by means of transmittance and reflectance spectra. The real (n) and imaginary (k) parts of the complex refractive index and dielectric constant of the thin film were determined. The oscillator energy E_o, dispersion energy E_d and other parameters have been determined by the Wemple–DiDomenico method. The optical band gap E_g was determined and the optical absorption spectra show that the absorption mechanism is a direct transition. The most significant result of the present study is to determine optical constants and optical band gap of the thin film.

Keywords: polymer, thin film, optical constants, optical band gap.

1. Introduction

Ionic polymers or ionomers basically contain a small percentage of ionic groups attached to a hydrocarbon backbone. The ionic interaction between the groups results in significant changes in polymer properties [1–3]. The development of polymeric systems with ionic conductivity is one objective in polymer research. Generally, ionic conduction in polymer electrolytes is dominated by the amorphous elastomeric phase [4]. Two major issues are charge carrier generation and transport, the latter is especially difficult to interpret. Although there are several models describing the origin and nature of charge carriers on polymer chains which take into account the specific electronic structure of a given polymer, the lack of long range order in most polymer systems does not allow to extend such treatments to completely describe their actual macroscopic electronic properties [5–7].

Although polymer electrolytes based on polymer-salt complexes are an important class of solid electrolytes due to some of their unique properties [2, 8], their low value of conductivity restricts their use in solid state batteries and electrochromic display devices. Plasticizers are added to polymer electrolytes to improve their mechanical and thermal properties, whereas the addition of dispersed second-phase particles is generally used to enhance their conductivity value [9]. In the field of optical devices, polymers are very effective for creating complex integrated optical devices. So, the aim of present study is to determine basic optical properties and optical constants of the ionomer thin film.

2. Experimental

2.1. Preparation of the ionomer

Synthesis, characterization and biological activity of 3-(1-cyclohexyl) azetidinyl methacrylate monomer and its homopolymer were described elsewhere [10]. In this study, the ionomer of poly(CyAMA) was prepared as follows: a quantity of homopolymer (1 g, 4.5 mmole) was put to a reaction tube which is 100 ml and it was dissolved in THF. 0.8 ml methyl iodide (0.0128 mmole) by a distillation funnel was distilled drop by drop, while solution was stirred by magnetic stirring. Reaction was made for 5 min. The mixture was precipitated in n-hexane and washed by ethyl acetate. Product was dissolved in DMS and was precipitated in ethyl acetate and then dried at 45°C. The prepared ionomer was named as poly(CyAMA)i. The film of the ionomer was prepared by evaporating the solvent from a solution of the ionomer with subsequent drying of the film deposited on quartz substrate. The solution of the ionomer was homogenized for 4 hours and was rotated for homogeneous mixing. From the optical spectral curves, the average thickness of the film was calculated according to the methods presented in literature in which transmittance and reflectance spectrums are used to obtain film thickness of the thin film [11], and was found as 150 ± 0.021 nm.

2.2. Measurements

IR analysis was performed using a Mattson 1000 FT-IR spectrometer. ^{13}C-NMR spectra were recorded on a Jeol FX-90 Q MHz spectrometer. The UV-Visible spectra of the ionomer prepared as a thin film were recorded by Shimadzu UV-12080 UV/Visible spectrophotometer at room temperature. The optical absorption and reflectance spectra were analyzed to determine the optical constants such as refractive index n, extinction coefficient k, and absorption coefficient α. Analysis of the absorption coefficient was also carried out to determine the optical band gap and nature of transitions.

2.3. Characterization studies

Infrared spectroscopy was used to characterize the structure of the ionomer. The characteristic IR absorption bands of the ionomer are at 1160 cm^{-1} (C–O–C), 1490 cm^{-1} (C–H), 1735 cm^{-1} (C=O), 2870–2890 cm^{-1} (C–H). The characteristic peaks at ^{13}C-NMR spectra of the I4 ionomer ($CDCl_3$ as solvent): 176.7 ppm (C=O), 68.87 ppm ($N^+–\underline{C}H_2$, azetidinyl ring), 63.7 ppm ($O–CH_2$), 60.8 ppm ($N^+–\underline{C}H_3$). The chemical structure of ionomer was confirmed by these characteristic signals [12].

3. Results and discussion

3.1. Refractive index dispersion

The transmittance and reflectance spectra of the thin film are given in Figure 1. The refractive index of the thin film was calculated from the following equation [11]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{1}$$

where k is the extinction coefficient and is calculated using formula $k = \alpha\lambda/4\pi$. The values of n and k were calculated and are shown in Fig. 2. The refractive index n

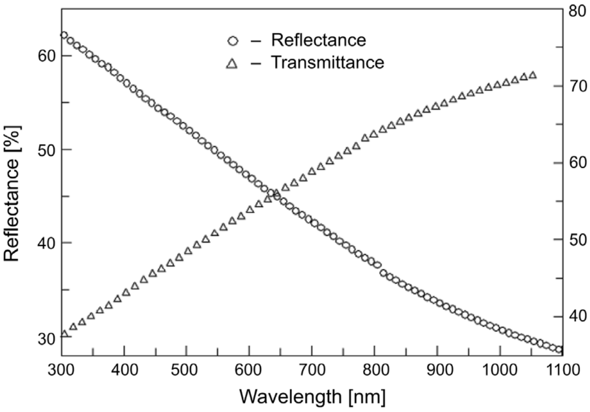

Fig. 1. Transmittance and reflectance spectra of the thin film.

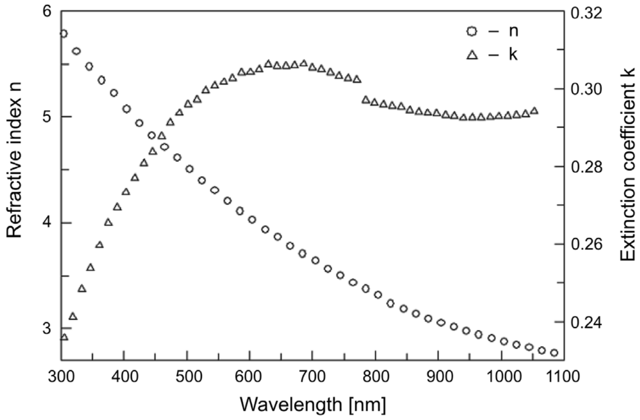

Fig. 2. Variation of the refractive index and extinction coefficient with wavelength.

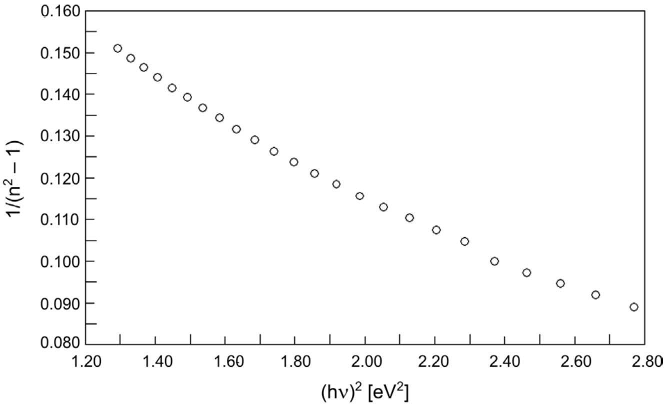

Fig. 3. Plot of $1/(n^2 - 1)$ *vs*. $(h\nu)^2$ for the thin film.

decreases with increasing wavelength, while the k value increases with wavelength and after certain point is decreased. The large values of n indicate also that the compound is absorbing. The variation of n and k values in investigated frequency range shows that some interactions take places between photons and electrons. The refractive index changes with the variation of the wavelength of the incident light beam due to these interactions. The refractive index dispersion of the thin film is expressed as [13]:

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2} \tag{2}$$

where n is the refractive index, h is Planck's constant, ν is the frequency, $h\nu$ is the photon energy, E_o is the average excitation energy for electronic transitions and E_d is the dispersion energy which is a measure of the strength of interband optical transitions. The dielectric response for transitions below the optical gap is described by this model. E_o and E_d values were calculated from the slope and intercept on the vertical axis of plot of $1/(n^2 - 1)$ versus $(h\nu)^2$ (Fig. 3) and are given the Table. The refractive index can be also analyzed to determine the long wavelength refractive index n_∞ and average oscillator wave length λ_o and oscillator length strength S_o of the thin film. These values can be obtained using the single term Sellmeier oscillator [14]

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 . \tag{3}$$

We obtained n_∞ and λ_o values from the linear parts of $1/(n^2 - 1)$ versus λ^{-2} and are given in the Table. Equation (3) can be rewritten as ($n_\infty^2 = 1 + S_o\lambda_o^2$) [15]

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1 - \lambda_o^2/\lambda^2} . \tag{4}$$

T a b l e. Optical parameters of the ionomer thin film.

E_o [eV]	E_d [eV]	E_g [eV]	n_∞	λ_o [nm]	E_o/S_o [eVm^2]	S_o [m^{-2}]
2.11	10.10	2.54	5.91	587.67	1.48×10^{-13}	1.42×10^{13}

The S_o value for the thin film was calculated and is given in the Table. The value of E_o/S_o was found as 1.48×10^{-13} eVm^2 for the thin film and this value is approximately of the same order as that obtained by DiDomenico and Wemple [13] for a number of materials.

3.2. Determination of the optical band

To determine the nature of the optical transitions, the optical absorption study was performed for the thin film. The optical absorption coefficient was calculated from the transmittance spectra of the thin film [11]. The optical absorption dependence of the photon energy is expressed by the following relationship [16]:

$$\alpha h\nu = A\left(h\nu - E_g\right)^m \tag{5}$$

where A is an energy-independent constant, E_g is the optical band gap and m is a constant which determines the type of optical transition ($m = 1/2$ and $3/2$ for direct allowed and forbidden transitions, respectively, $m = 2$ and 3 for indirect allowed and forbidden transition, respectively). The type of transition can be obtained finding the value of m. For this, Eq. (5) can be written as

$$\ln(\alpha) = \ln(A) - \ln(h\nu) + m\ln(h\nu - E_g). \tag{6}$$

If E_g is known, the value of m can easily be obtained from the slope of $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$. Rearranging of Eq. (6), one obtains,

$$\frac{\mathrm{d}\left[\ln(\alpha)\right]}{\mathrm{d}\left[h\nu\right]} = -\frac{1}{h\nu} + \frac{m}{h\nu - E_g} \tag{7}$$

The curve of $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ was plotted to determine value m. Value m is found to be about 1/2 which shows an electronic transition from the valence band to the conduction band and strong electronic absorption. Thus, a more precise value was obtained from the linear part of the $(\alpha h\nu)^2$ versus $h\nu$ (Fig. 4) and is given in the Table.

3.3. Complex dielectric function

The complex dielectric constant ($\varepsilon^* = \varepsilon_r + i\varepsilon_i$) characterizes the optical properties of a solid material. The real and imaginary parts of dielectric constant were also determined by the following relations [17]:

$$\varepsilon_r = n^2 - k^2 = \varepsilon_\infty - \frac{e^2}{4\pi^2 c^2 \varepsilon_o} \frac{N}{m^*} \lambda^2 \tag{8}$$

and

$$\varepsilon_i = 2nk = \frac{\varepsilon_\infty \omega_p^2}{8\pi^2 c^3 \tau} \lambda^3 \tag{9}$$

where ω_p is the plasma frequency, ε_∞ is the high frequency dielectric constant, e is the electronic charge, N is the free carrier concentration, m^* is the effective mass of the free carrier, τ is the optical relaxation time, c is the velocity of light. The real and

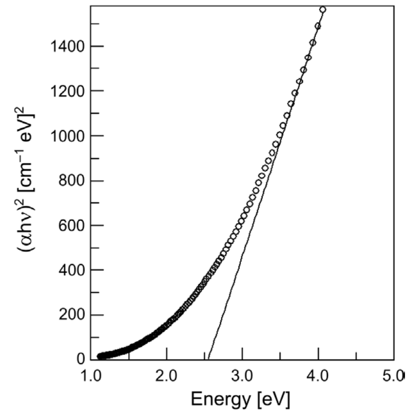

Fig. 4. Plot of $(\alpha h\nu)^2$ *vs.* $h\nu$ for the thin film.

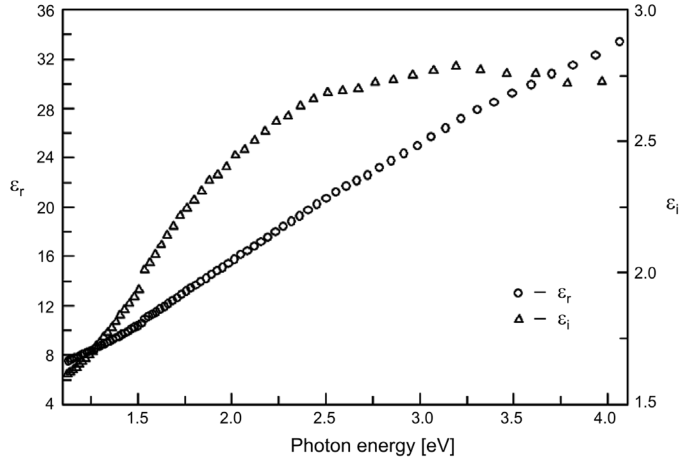

Fig. 5. ε_r and ε_i *vs*. photon energy plots for the thin film.

imaginary parts of the dielectric constant were calculated using Eqs. (8) and (9) and are shown in Fig. 5. It is seen that the real and imaginary parts of the dielectric constant increase with increasing photon energy. The real part of the dielectric constant is higher than the imaginary part.

4. Conclusions

The basic optical properties and optical constants of the ionomer thin film have been investigated by means of transmittance and reflectance spectra. The optical constants such as the real (n) and imaginary (k) parts of the complex refractive index, the real part and imaginary parts of the dielectric constant, and optical band gap of the thin film were determined. The oscillator energy E_o, dispersion energy E_d and other parameters have been determined by the Wemple–DiDomenico method. The optical band gap was determined and the optical absorption spectra show that the absorption mechanism is a direct transition.

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