STUDY OF THE OPTICAL PROPERTIES OF POLY (METHYL METHAACRYLATE) (PMMA) DOPED WITH A NEW DIARYLETHEN COMPOUND

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ABSTRACT

The optical characteristics of poly (methyl methacrylate) (PMMA) films doped with4-(5-{2-[5-(4-Cyanophenyl)-3-methylthiophen-2-yl]-3,3,4,4,5,5-hexafluorocyclopent - 1-en-1-yl}-4-methylthiophen-2-yl) benzonitrile (I) were studied . The polymer films were prepared using solution casting technique, different concentrations (0, 2.0, 4.0 and 6.0 wt %) of the dopant (I) were used and the optical properties of the prepared films were investigated. The optical absorption spectra of these films in the wavelength range from 190-890 nm were measured to investigate the influence of I on the optical properties of PMMA. The results showed that Energy gap (Eg_{opt}) of the polymer films decreases with increasing I concentration. The absorbance, absorption coefficient, extinction coefficient, finesse coefficient, refractive index, parts dielectric constant (real and imaginary) and optical conductivity of the prepared PMMA films were found to be increased with increasing the concentration of I. The indirect optical band gap for the pure and the doped PMMA films were estimated to be about 2.6, 2.8, 3, and 3.2eV for indirect allowed transition , whereas the indirect forbidden band gaps were determined as 2.5, 2.6, 2.7 and 3.2 eV with increase(I) contents, respectively.

Keywords: Poly (methyl methacrylate), methylthiophen, diarylethen

INTRODUCTION

Photochromic compounds are important compounds because of their potential applications in optical memories and molecular switches,(1,2). a big number of diarylethenes with heteroaromatics (especially diarylperfluorocyclopentenes with thienyl groups) has been developed, and the development in this field is still ongoing. The uses these compounds in manufacturing the optical memory, molecular switches, computers, data storage (write and read) and other optical devices stand in need for the material to be in solid films. Photochromic diarylperfluorocyclopentene polymers are favoured over low molecular weight monomeric compounds, accordingly, the photochromic polymers became interesting materials.(3) The most convenient method for making photochromic polymers (films) is to embed the diarylethene compounds into a polymer matrix.(3-4) One of the commonly used polymers for such purposes is poly(methyl methacrylate) (*PMMA*). Films can be prepared by a spin coating technique or by making a solution of a mixture of the PMMA and the photochromic diarylethene followed by casting the mixture on a cover glass and drying.(5) In the present work the effect of a novel diarylethene compound as a dopant on the optical properties of PMMA is studied.

EXPERIMENTAL

Materials

Poly (methyl methacrylate) **(PMMA)** films doped with (**I**) were prepared by solution casting technique, mixtures of the PMMA and **I** in 0, 2.0, 4.0 and6.0 wt% were dissolved in glass

beaker (30 ml) by chloroform using magnetic stirrer and placed in Petri dish 5cm diameter (the Petri dishes were cleaned with water using ultrasonic device). After evaporation of the solvent, samples were dried in oven at 50^OC for 2 h .The thickness of the dried samples were measured using micrometer.The spectra of absorption and transmittance were recorded for wavelengths 190-890 nm using double beam spectrophometer UV-Vis- CECIL 2700, provided by optima 300 plus company.

Theoretical

The relationship between incident intensity(I) and penetrating light intensityI_0 is given by Equation 1 (*6*):

$$I = I_0 e^{-\alpha t} \ \ldots\ldots\ldots \ (1)$$

Where t is the thicknesses of matter (cm) and α is the absorption coefficient (cm)$^{-1}$.

$$\alpha t = 2.303 \log \frac{I}{I_0} \ \ldots\ldots\ldots \ (2)$$

Where the amount of $\log \dfrac{I}{I_0}$ represents the absorbance (*A*).

The absorption coefficient can be calculated by:

$$\alpha = 2.303(A/t) \ \ldots\ldots\ldots \ (3)$$

If the amount of absorption is $\alpha \geq 10^4 cm^{-1}$ the electronic transitions are direct. The amount of optical energy gap from this region can be evaluated by the relation (*7*):

$$\alpha h\upsilon = A(h\upsilon - E_g)^m \ \ldots\ldots\ldots \ (4)$$

Where $h\upsilon$ is the photon energy, (*A*) is the proportional constant, E_g is the allowed or forbidden energy gap of direct transition and m is a constant.

The refraction index consists of real and imaginary parts$(N = n - ik)$, the relation between reflectivity and refractive index is given by (8):

$$R = \frac{(n-1)^2 + k^2}{(n-1)^2 + k^2} \ \ldots\ldots\ldots \ (5)$$

Where k is the extinction coefficient, *R* is reflectivity and *n* is refraction index.

The absorbance and transmittance can be calculated by the following Equation:

$$R + A + T = 1 \ldots\ldots\ldots \ (6)$$

Where *T* is transmittance

The refractive index can be expressed by: (8)

$$n = \sqrt{\frac{4R - k^2}{(R-1)^2} - \frac{(R+1)}{(R-1)}} \ldots\ldots\ldots \ (7)$$

The extinction coefficient can be calculated by: (8)

$$k = \frac{\alpha\lambda}{4\pi} \ \ldots\ldots\ldots \ (8)$$

Where λ is the wavelength of the incident ray.

The relation between the complex dielectric constant and the complex refractive index N is expressed by:

$$\varepsilon = N^2 \quad \ldots\ldots\ldots (9)$$

It can be concluded that: (6)

$$(n - ik)^2 = \varepsilon_1 - i\varepsilon_2 \quad \ldots\ldots\ldots (10)$$

The real and imaginary complex dielectric constant can be expressed by Equation 11 and 12, respectively:

$$\varepsilon_1 = n^2 - k^2 \ , \varepsilon_2 = 2nk \quad \ldots\ldots\ldots (11)$$

Also, the finesse coefficient is given by: (6)

$$F = \frac{4R}{(1-R)^2} \quad \ldots\ldots\ldots (12)$$

The optical conductivity is related to light speed and can be expressed by the following equation:(6)

$$\sigma_{opt} = \frac{nc\alpha}{4\pi} \quad \ldots\ldots\ldots (13)$$

RESULTS AND DISCUSSION

Figure (1) shows the absorbance spectra as function of the wavelength of the incident light for PMMA film with different concentration of **I**. It is clear that increasing the concentration of **I** in the polymer matrix leads to increasing the peak intensity, and there is no any shift in the peak position for all amounts of the added material (**I**) to the polymer, that means there is no chemical interaction between the two components in the matrix and the increment in the absorption is attributed to the increment of the concentration of **I** which is the absorbing component.
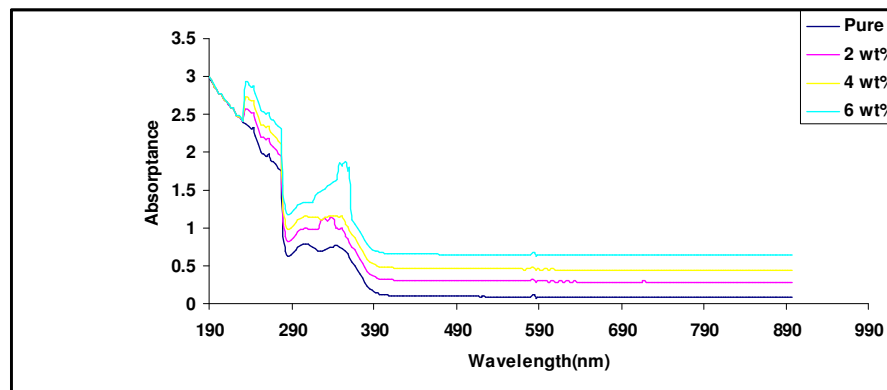

Figure 1. The absorbance spectra of (PMMA- I) composites as function of incident light wavelength

Figure(2) shows the optical transmittance spectra as function of wavelength of incident light for several concentration of the added ions ,the polymer transmittance decrease with the increasing the concentration of **I**, this is due to the added (**I**) molecules that contains in it is outer orbits, these electrons absorb the electromagnetic energy of the incident light ,then, as a result electrons excited to higher energy levels, this process is not accompanied by emission

of radiation because the electron that moved to higher levels have occupied vacant positions of energy bands ,thus part of the incident light is absorbed by the substance and does not penetrate through it ,on the other hand the pure Poly (Methyl Methacrylate) **(PMMA)**has high transmittance because there are no free electron (i.e .electrons are strongly linked to them atoms through covalent bonds) ,i.e. the breaking of electron linkage and moving to the conduction band need photon with high energy *(9).*
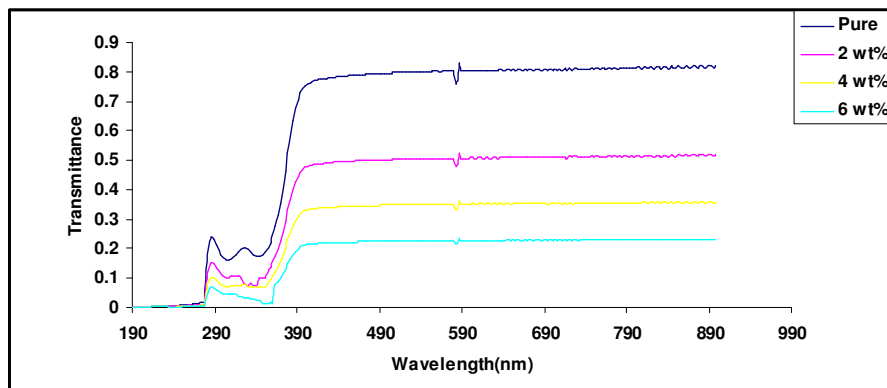

Figure 2. The Transmittance spectra of (PMMA-I) composites as a function of incident light wavelength

The absorption coefficient (α) is calculated using equation (3). Figure (3) shows the absorption coefficient (α) as a function of the photon energy, it can be noted that absorption is relatively small at low energy. This means that the possibility of electron transition is low, because the energy of the incident photon is not sufficient to move the electron from the valence band to the conduction band ($h\upsilon < E_g$)**.**

At high energies, absorption is high ,this means that there is a great possibility for electron transitions consequently, where the energy of incident photon is enough to move the electron from the valence band to conduction band ,this means that the energy of the incident photon is greater than the forbidden energy gap *(9)* .This shows that the absorption coefficient assists in figuring out the nature of electron transition ,when the values of the absorption coefficient is high ($\alpha > 10^4$) cm^{-1} at high energies, it is expected that direct transition of electron occur ,the energy and moment are maintained by the electrons and photons ,on the other hand when the values of the absorption coefficient is low ($\alpha < 10^4$)cm^{-1} at low energies ,it is expected that indirect transition of electron occur ,and the electronic momentum is maintained with the assistance of the phonon *(10)*. Among other results is that the coefficient of absorption for the PMMA in the presence of **I** as dopant is less than 10^4 cm^{-1}, this explains that the electron transition is indirect.
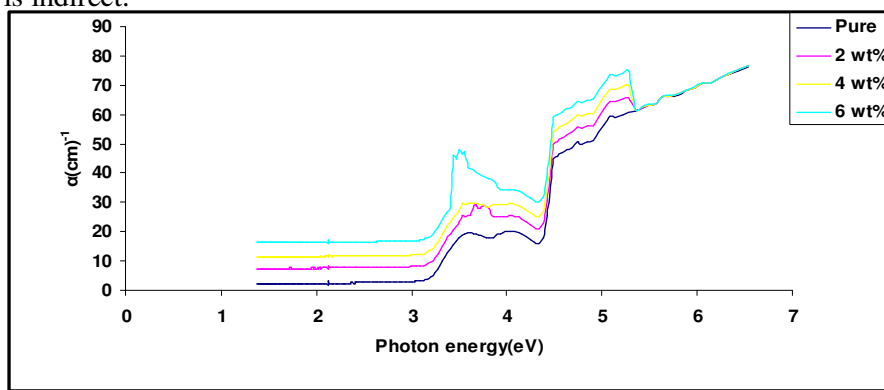

Figure 3.The absorption coefficient of (PMMA-**I**) as a function of photon energy

Figure (4) shows the relationship between absorption edges $(\alpha h \upsilon)^{1/2}$ for casting material as a function of photon energy. At extension of the curve to the values of $(\alpha h \upsilon)^{1/2} = 0$, we get indirect allowed gap transition.

From Figure (5), we see that the values of energy gap decrease with increase of the weight percentage of **I**. These attributes to the creation of the site levels in forbidden indirect energy gap lead to facilitate the crossing of electron from the valence band to the local levels to conduction band *(11)*. In other meaning the electronic conduction depends on added impurities.
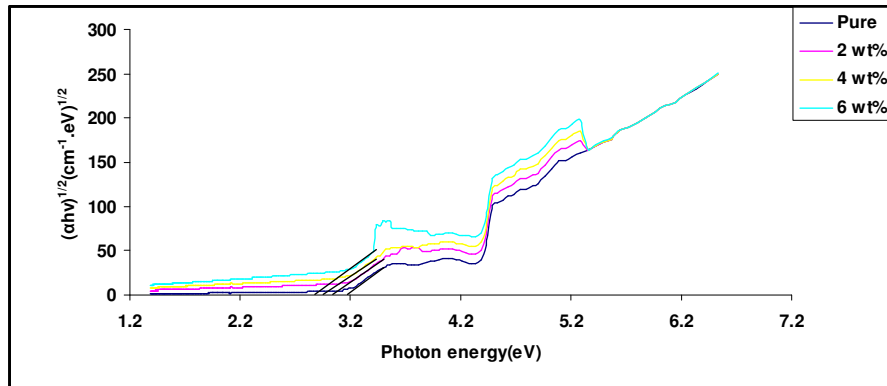
Figure 4. $(\alpha h u)^{1/2}$ vs. $h\upsilon$ plot of doped PMMA films for different dopant concentrations with energy of allowed indirection transitions
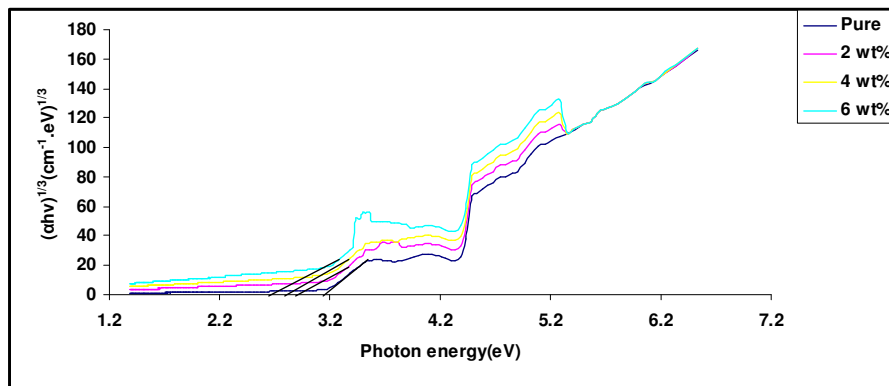

Figure 5. $(\alpha h u)^{1/3}$ vs. $h\upsilon$ plot of doped PMMA films for different dopant concentrations with energy of forbidden indirection transitions

Figure (6) describes the change in refraction index for (PMMA-**I**) as a function of wavelength that has occur red due to an increase in n with increasing the doping percentage. This is because pure PMMA is an amorphous crystalline substance with low density that increases with increasing the concentration of **I**. The refraction index decreases at the greatest wavelengths and increases at greatest dopant concentration, because the transmission of the longest wavelength is more.

The change of extinction coefficient as a function of wavelength is shown in Figure (7). It was noted that k has lower value at low concentration, and this is attributed to increase in the absorption coefficient with increased doping percentages of added salt ions. The extinction coefficient is high at the longest wavelengths and high concentration
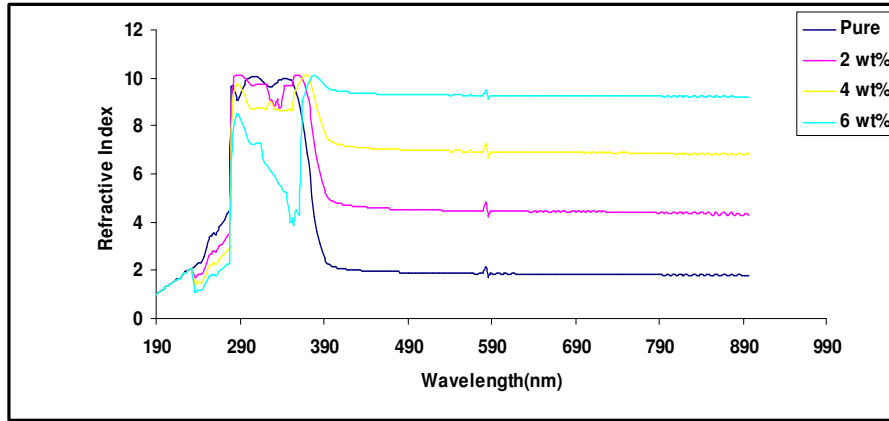
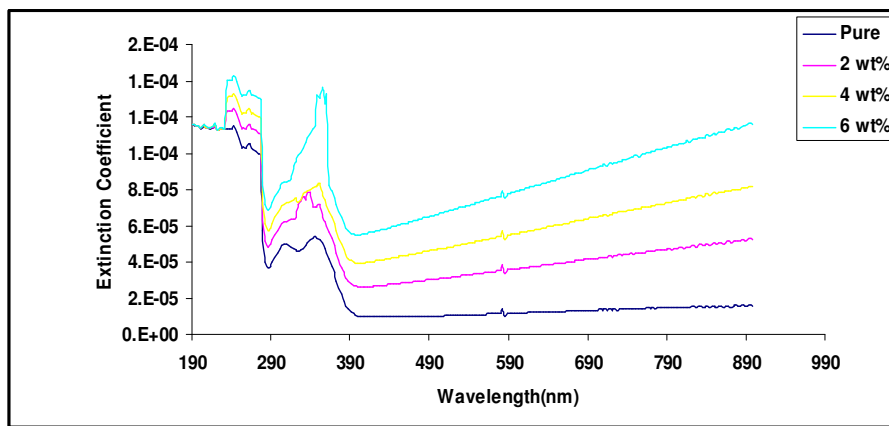Figure 6. The refraction index of PMMA-**I** films as a function wavelength at different concentrations

Figure 7. The extinction coefficient of PMMA-**I** films as a function wavelength at different concentrations

The real dielectric depends on n^2 and k^2 but the imaginary dielectric depends on k and n. The real and imaginary dielectric constant(ε_1 and ε_2) for (PMMA-**I** have been calculated from Equation (11),Figures (8) and (9) show the change of these constants with wavelengths .The values of the real dielectric constant are high with respect to the imaginary dielectric constant, because they are dependent on n and k values.
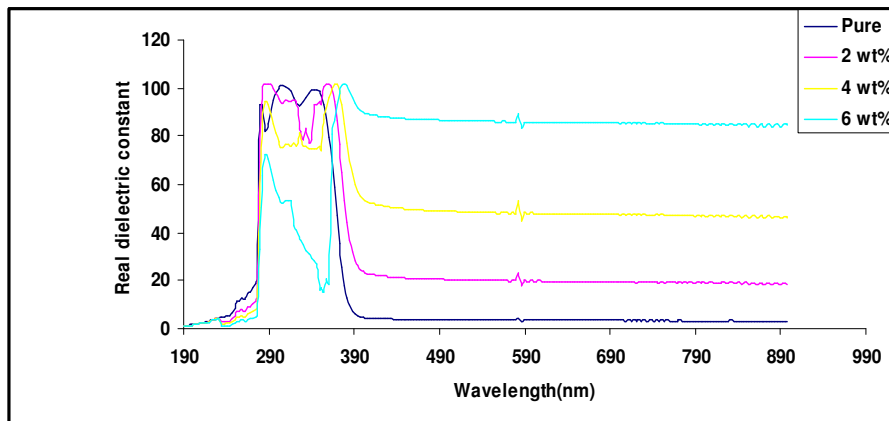

Figure 8. The real dielectric constant of PMMA-**I** films as a function wavelength at different concentrations
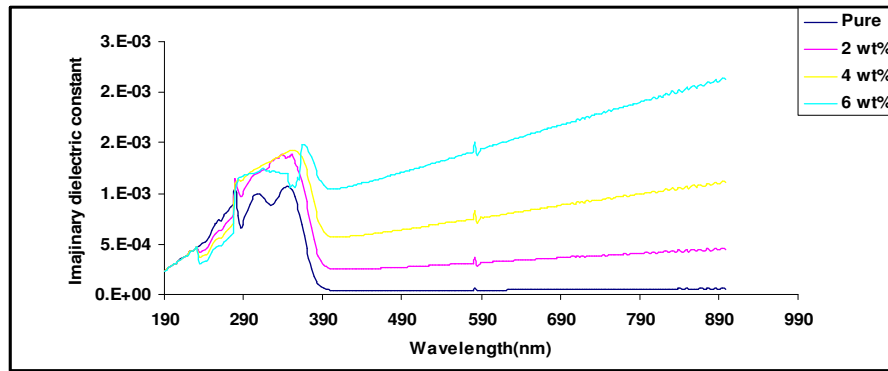
Figure 9. The imaginary dielectric constant of PMMA-**I** films as a function wavelength at different concentrations

Figure (10) shows the values of finesse coefficient against wavelengths at different concentration of PMMA-**I**. It was observed that *F* values decreases at 190 to 376 nm wavelengths. The position of the peaks spectrum is slightly shifted especially at the greatest concentration of doping. This means that there is a little change in polymer structure as a result of doping. Also, the finesse coefficient increases with increasing in doping percentage because of doped additives that lead to changing in reflectance which F is dependent on R, as described in Equation (12).

The optical conductivity decreases suddenly after 200 nm wavelength as shown in Figure (11). It was observed an increase in optical conductivity as increasing in doping percentages. This means that the generation of (**I**) ions percentages increases the contribution of electron transitions between the valence and conduction bands, which lead to reduction of energy gap as a result of sit level generation. This optical conductivity becomes constant after 400 nm.
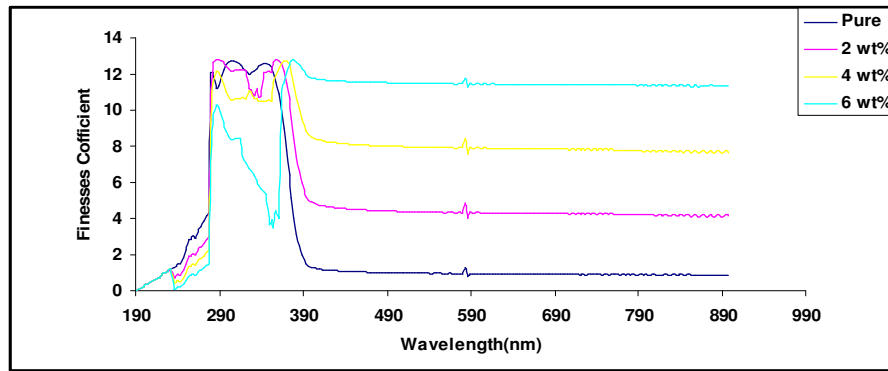

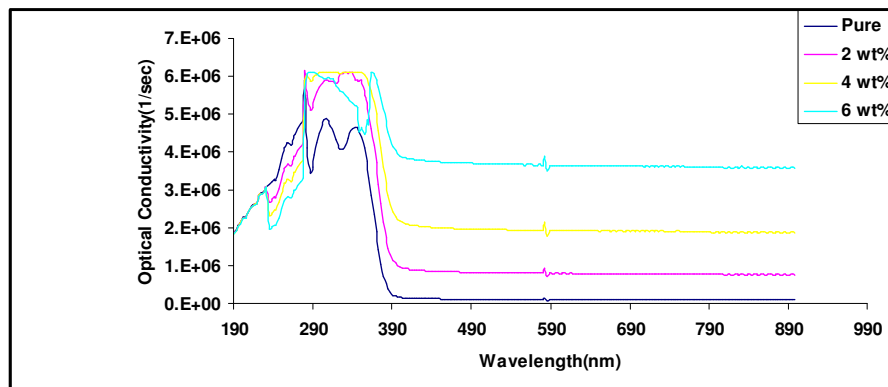Figure 10. The finesse coefficient as a function of wave length for PMMA-**I** films

Figure 11. The optical conductivity as a function of wave length for PMMA-**I** films

CONCLUSION

The absorbance, absorption coefficient, extinction coefficient, finesse coefficient, refraction index and reflectance of the PMMA films doped with a new diarylethene compound (**I**) where found to be increasing with the increasing of doping concentration. The energy gap of indirect transition decreases with increasing the concentration of the dopant. The dielectric constant (real and imaginary) was also found to be increasing with increasing the concentration of the dopant.

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