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Preparation Polysulfide Polymer containing 1, 3, 4-thiadiazole unit and Study of Its Optical Properties.

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ABSTRACT

Polymeric sulfides containing 1, 3, 4-thiadiazole unit (M) with different spacer group length have been synthesized. The optical properties of the prepared polymers have been examined. The transmittance, reflectance, absorption coefficient, extinction coefficient, refractive index, dielectric constant (real and imaginary) and optical connectivity as optical properties had been measured. The results has shown that all these properties are increased with increasing the concentration except the transmittance, it decreases with increasing the concentrations. While, those properties are decreased with increasing wavelength values except the transmittance, it increases with increasing wavelength.

Keywords: polymeric sulfide, 1, 3, 4-thiadiazole, Optical properties, Absorption coefficient.

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INTRODUCTION

Sulfur compounds play important role in Industrial and medical applications [1,2] Poly(alkylene sulfides) are important polymers and their applications have been reviewed recently [3], Also, we report the use of two poly(alkylenedisulfides) and poly(alkylene sulphides) containing 1,3,4-thiadiazol units as catalysts, with the aim to enhance para selectivity in chlorinations of various phenols[4,5]. The ionic conductivities of poly(alkylene sulphides).AgNO3 electrolytes are comparable to those of poly(ethylene oxide) PEO-alkali metal salts [6]. Therefore, they synthesis of such polymers are always of interest.

Poly(alkylene sulfides) are usually prepared by one of four major methods: the polymerization of episulfides, reactions of dithiols with carbonyl compounds, addition of thiols to diolefins, and reactions of dithiols with dihalides. The first two obviously apply to only very specific types of polymeric sulfides, while the other two methods are not simple to operate.

Work carried out by our research group to synthesise a range of polyalkylene sulphides [7]. We have been able to produce a range of polymers simply from reactions of dihaloalkanes with cheap sodium sulfide nanohydrate by use of reflux conditions for (2-4) h in the absence of a catalyst or additional solvent. The process has been applied for dihaloalkanes with chain lengths from 2 to 8 carbons and generally gives high yields (>97 %). In this paper we report the high yielding synthesis of a range of polyalkylene sulphides.

Heterocyclic moieties can be found in a large number of compounds which display Industeral applications. The activity of the compounds is mainly dependent on their molecular structures [8]. 1, 3, 4-thiadiazoles are very interesting compounds due to their important applications in many pharmaceutical, biological and analytical field [9,10].

Theoretical Part

The study of the optical properties of polymers increases our knowledge of the type of polymer internal structure, nature of the bonds and expands the potential scope of polymer application. Polymers provide remarkable advantages in optical applications over common inorganic glasses, especially with respect to their light weight, impact and shatter resistance [11, 12]. Absorbance (A) defined as the ratio between absorbed light intensity (I) by material and the incident intensity of light (I_o) [13].

$$A = \log \frac{I}{I_o} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where absorbance was measured by using a device (UV-Spectroscope), The ratio (I / I_o) called (Transmittance) (T_r), so can be defined as the ratio of the intensity of the transmitting rays (I) through the film to the intensity of the incident rays (Io) on it as follows and connected by absorbance as [14]:

$$T_r = e^{-2.303A} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Reflectance (R) can be obtained from absorption and transmission spectrum in accordance to the law of conservation of energy by the relation [15]:

$$R = 1 - A - T_r \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The light absorbance coefficient(α_{op}) and films absorption coefficient are given by the equation [16]:

$$\ldots\ldots\ldots\ldots\ldots\ldots (4) \qquad \alpha_{op} = 2.303 * \frac{A}{x}$$

Where (x) thickness of thin film.

The extinction coefficient (k) represents the amount of attenuation of an electromagnetic wave that is traveling in a material, where it values depends on the density of free electrons in the material and on the structure nature, so given by following equation [17]:

$$k = \alpha_{op}\lambda / 4\pi \qquad \text{……..………………………. (5)}$$

where (λ) is the wavelength of incident photon rays.

The refractive index (n) can be defined as a ratio between the speed of light in vacuum (c), to its speed of light in medium (v) and given by the relation [18]:

$$n = \frac{c}{v} \qquad \text{……………………….……… (6)}$$

The value of refractive index was calculated by using equation depending on the reflectance and extinction coefficient (k) as in the following equation [19,20].

$$\text{………………} \quad n = \left[\frac{(1+R)^2}{(1-R)^2} - \left(k^2 - 1\right)\right]^{1/2} + \frac{(1+R)}{(1-R)} \qquad (7)$$

The real dielectric Constant (ε1) it depends on the refractive index as in the following equation[21] :

$$\varepsilon_1 = n^2 - k^2 \qquad \text{………………………………(8)}$$

But imaginary dielectric Constant (ε2) it depends on the extinction coefficient as in the following equation [21] :

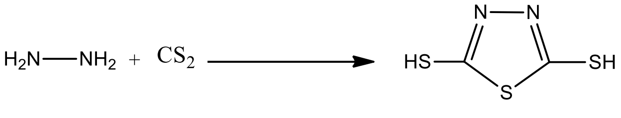
$$\varepsilon_2 = 2n\,k \qquad \text{……………………………….(9)}$$

Optical connectivity σ op is be found from the following equation is measured by unit (1/s)[20]:

$$\sigma_{op} = \alpha_{op}\, n\, c/4\pi \qquad \text{…………………………….(10)}$$

RESULTS AND DISCUSSION

The first task was to synthesize Polymeric sulfides containing 1, 3, 4-thiadiazole units with different spacer group length between the disulfide units. A mixture of hydrazine (99%), and carbon disulfide in pyridine was refluxed with continuous stirring for 5 hr. It was then filtered and the solvent was removed under reduced pressure. The residue was dissolved in distilled water, and acidified with conc. HCl to give a yellow precipitate. The crude product was filtered and recrystallized from ethanol as yellow needles (2,5-dimercapto-1, 3, 4-thiadiazole) (1; Figure(1)) in 90 % yield [22].



1 (90%)

Figure (1) Synthesis of 2,5-dimercapto-1,3,4-thiadiazole (1).

1H NMR spectrum a NH can be observed, representative of a thioamide (9.85 ppm) instead of a thiol (SH) group (2.0-4.0 ppm). It can therefore be concluded that compound 1 exists in its thione form in dimethyl sulfoxide solution. The FTIR spectrum of compound (1) showed a medium intensity band at 1624 cm^{-1} that could correspond with (C=N) stretching in the vicinity of 1,3,4-thiadiazole ring. In this spectrum there are two other characteristic bands at (3200 and 2550) cm^{-1} due to (N-H) and (S-H) stretching vibrations, respectively. From this we can say that this compound can exist in the thiol and thion form.

Poly sulfide polymers 1 was synthesized by dissolving Na in (25) mL of absolute ethanol followed by the simultaneous addition of compound 1, and the solution was heated. To the resulting boiling solutions benzene were added (45) mL and DCM. After the vigorous and spontaneous reaction subsided, (45) mL of benzene was added and the mixture was refluxed overnight. After mixture was cooled, it was filtered. The solution was evaporated under reduced pressure to give the corresponding polymeric sulfide Figure (2) in 67% yield [23].

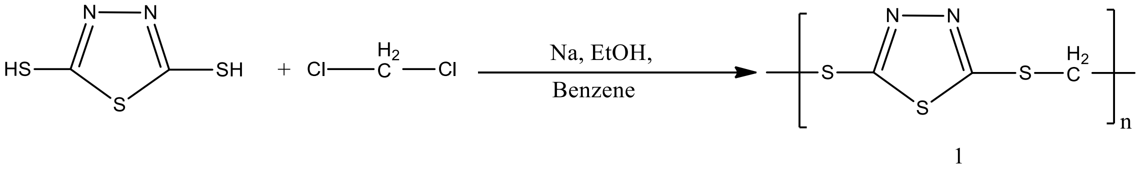


Figure (2) Synthesis of poly sulfide 1.

The number average molecular weight (Mn) of the polymer 3, measured by gel permeation chromatography (GPC), was found to be 6519, suggesting an average number of repeating units in the region of 16. The use of a polystyrene standard for the GPC may exaggerate Mn for a polymer with a totally different kind of repeating unit.

Poly sulfide polymer (2; 70% yield) was synthesized by a similar procedure except using 1, 2-dichloroethan instead of DCM Figure (3). The number average molecular weight Mn determined by GPC (6321) suggested that the average number of repeating units in the region of 14.

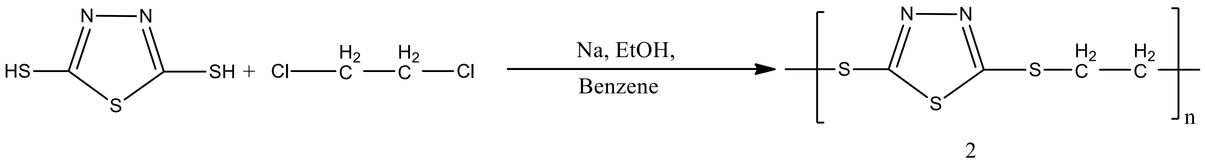


Figure (3) Synthesis of poly sulfide 2.

Absorbance

It was measured Absorbance of the preparator polymer films of the concentrations (0.1, 0.2, 0.3 and 0.4) g/mL %, as the figure (4) showes the spectrum Absorbance at room temperature as a function of the change in the wavelength of the range (200-1100) nm, note that the peack (Absorbance) increase as a result of the increase due to increased concentrations within range (300-380) nm, this applies with Lambert Beer Law, these filmss absorbs short wavelengths any high energies this is useful in applications of solar cells and detectors etc[24].

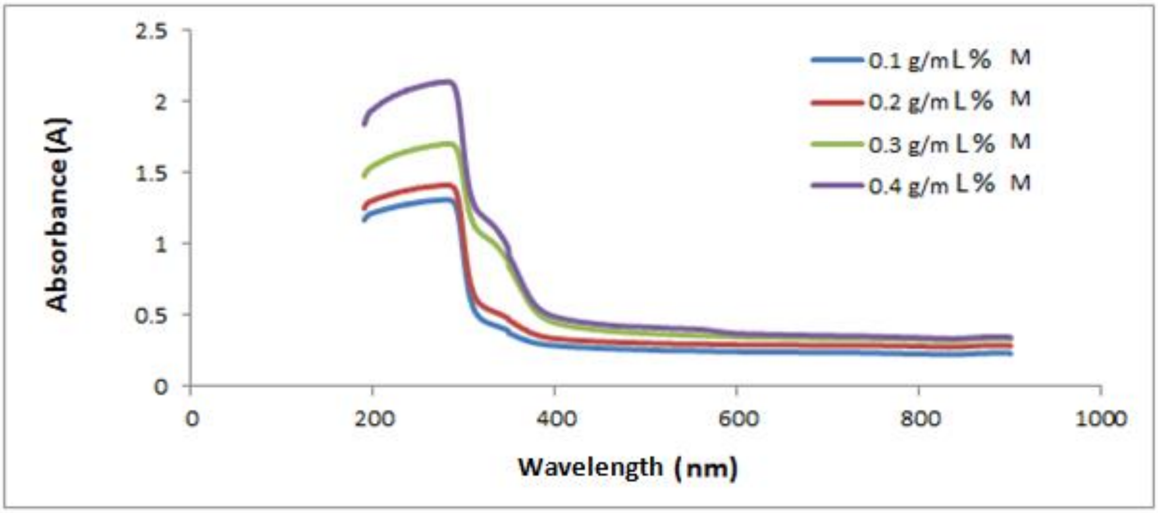


Figure (4) absorbance as a function of Wavelength

Transmittance

It has been found transmittance of the preparator polymer films of concentrations previously mentioned using equation (2) and the results showed increased transmittance values with increasing wavelength due to the decrease in absorbance values, when increasing the polymer concentration of the transmittance begins decreased because an inverse relationship between the absorbance and transmittance. From figure (5) we note that the polymer is a record high transmittance of the visible spectrum and less decrease of any wavelength in the ultraviolet region (UV-region)[25].

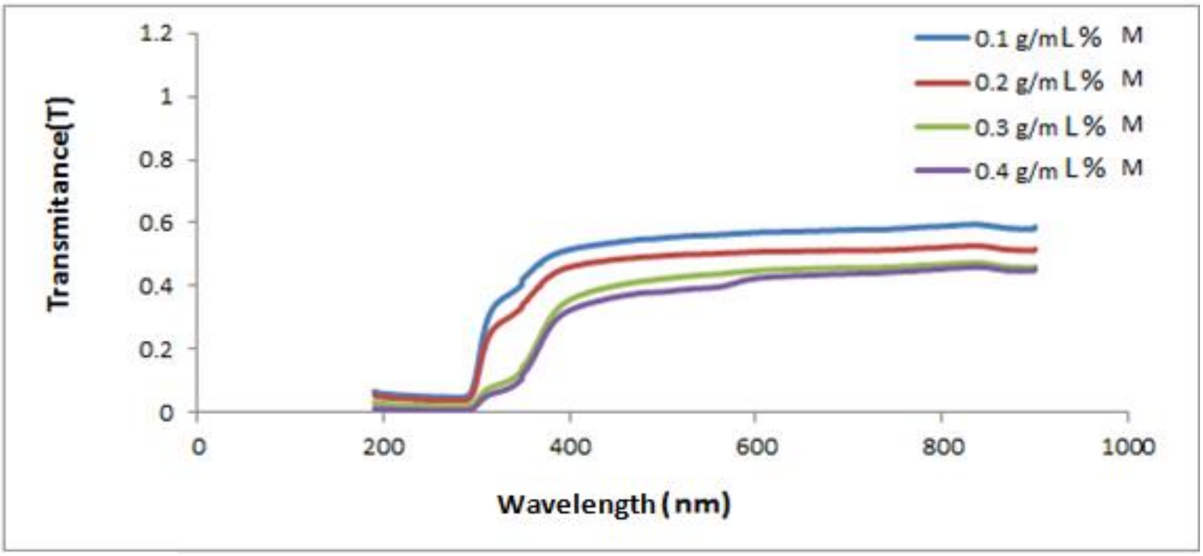


Figure (5) transmittance as a function of wavelength

Reflectance

Was finding the reflectance values from the equation (3). Figure (6) illustrates the spectrum reflectance as a function of wavelength of light falling on the of polymer films, we note that an increase of the concentration of the reflectance begins increase due to increased membrane intensity and reflectivity are high in certain of the spectrum over the ultraviolet and less with increase of any wavelength in the visible region (Vis- region) there is a reflective but a few[26].

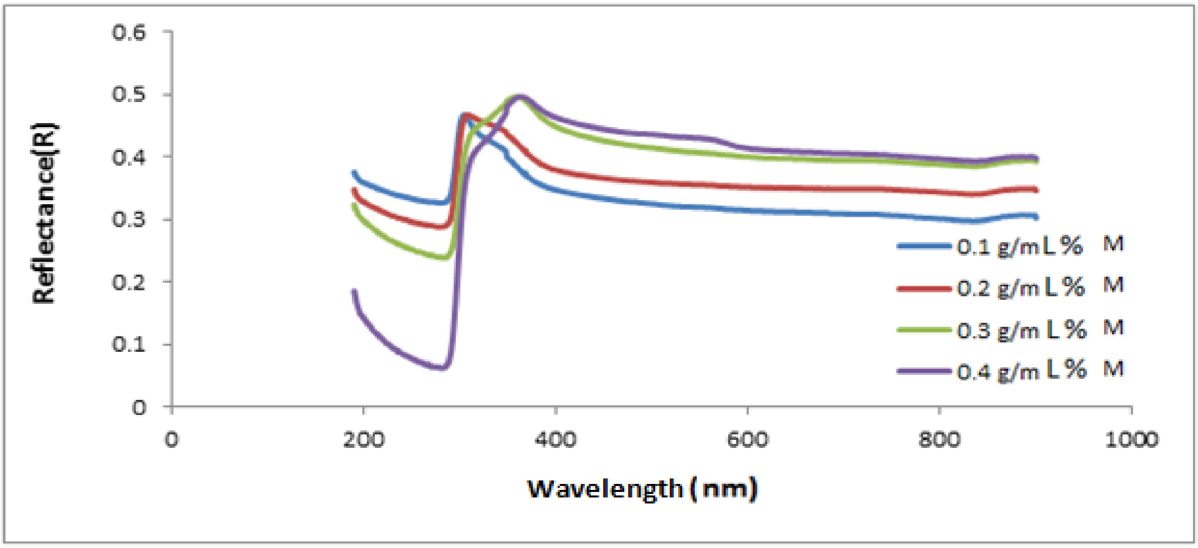


Figure (6) reflectance as a function of wavelength

Absorption coefficient

Has been found absorption coefficient values using equation (4) and figure (7) note absorption coefficient be of high value in the near ultraviolet region, indicating that these polymer films have the ability to UV absorption and the highest value of absorption at the wavelength is (300) nm, and increases the value of absorption coefficient increased as the concentration of molecules that absorb increasingly falling energy, thus increasing the value of the absorption coefficient [24,27].

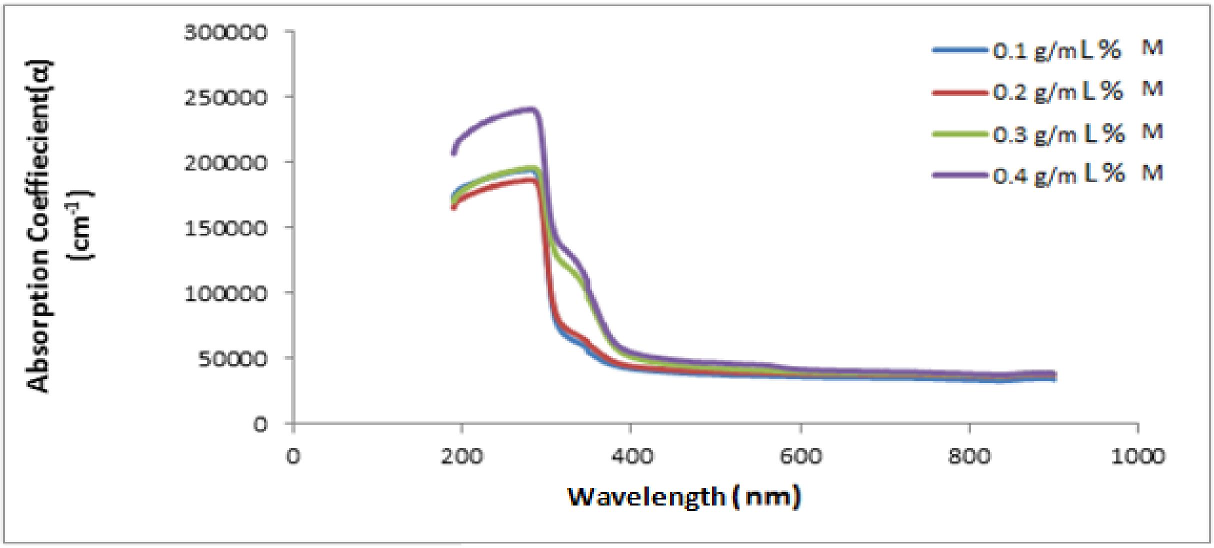


Figure (7) absorption coefficient as a function of wavelength

Extinction coefficient

It has been found extinction coefficient of relationship (5), and figure (8) observe in the ultraviolet region and in the few concentrations be extinction coefficient of high values and increases with concentration and to increasing absorption coefficient because the relationship between them is a positive, but in the visible region have slightly extinction coefficient and so
little in this area for absorption.

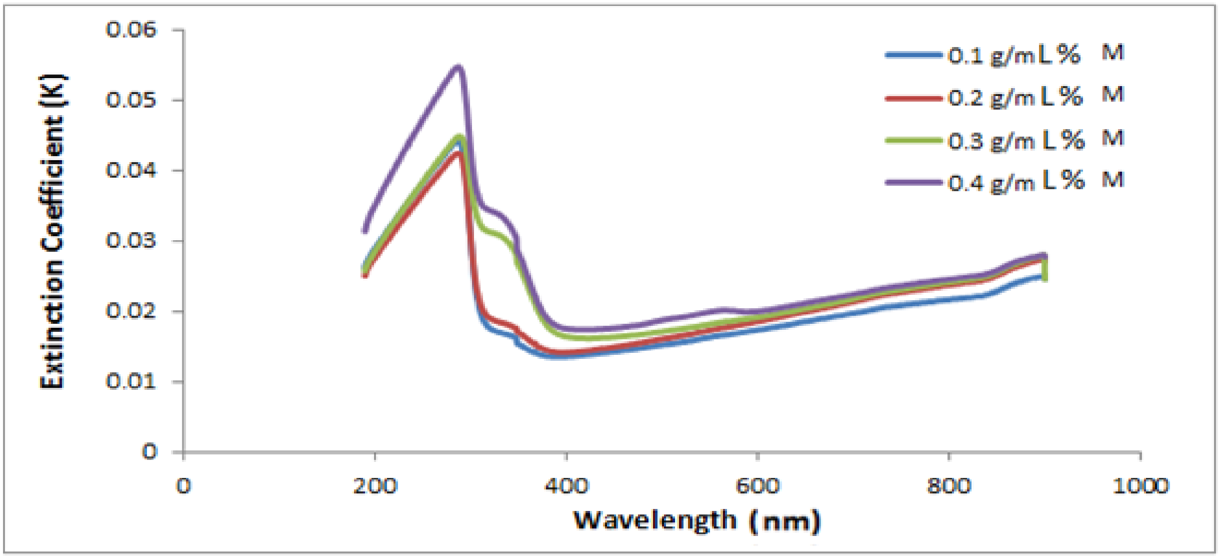


Figure (8) extinction coefficient as a function of wavelength

Refractive index

Was finding the refractive index values from the equation (7) and figure (9) note decreased refractive index values with increasing wavelength and increasing increase concentration and the reason for this is due to increasing the value of density and density is an important function to calculate the refractive index so increasing the values of the refractive index[28,29] .

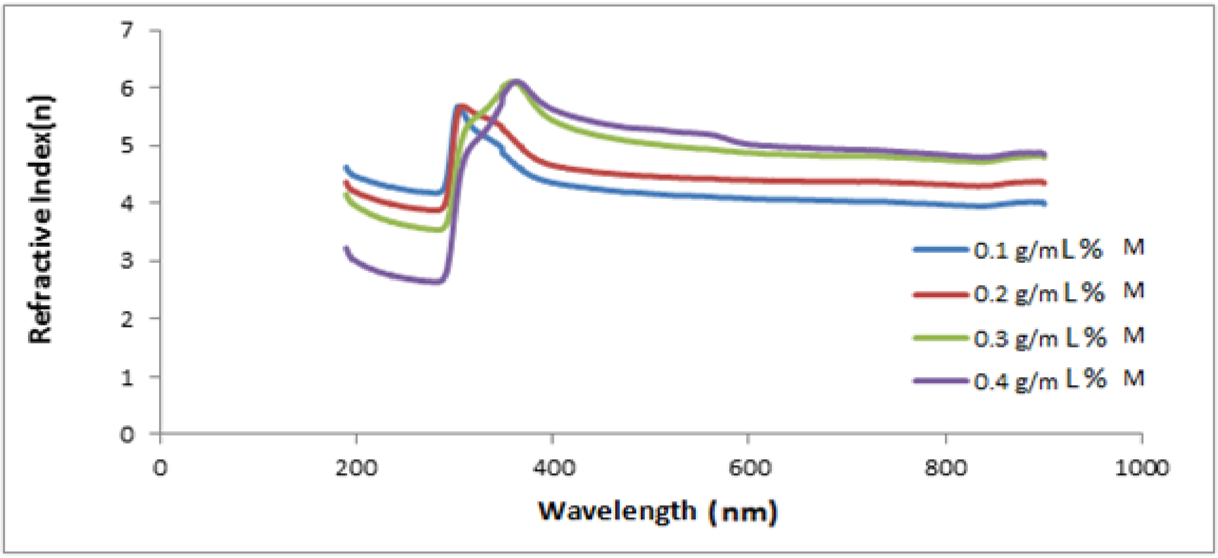


Figure (9) refractive index as a function of wavelength

Dielectric constant

The real and the imaginary dielectric constant calculation from relationships (8) and (9), respectively, and figure (10) note the real dielectric constant depends largely on the refractive index compared with the small square extinction coefficient values, while figure (11) shows the imaginary dielectric constant where we note that his behavior is somewhat similar to the behavior of extinction coefficient by previous relationship[30].

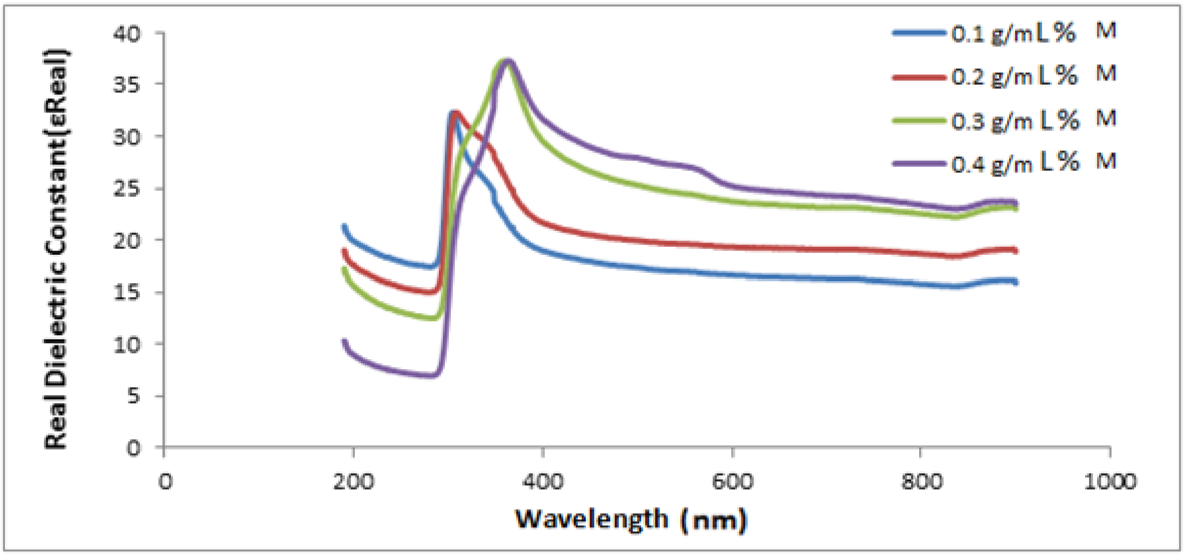


Figure (10) real dielectric constant as a function of wavelength

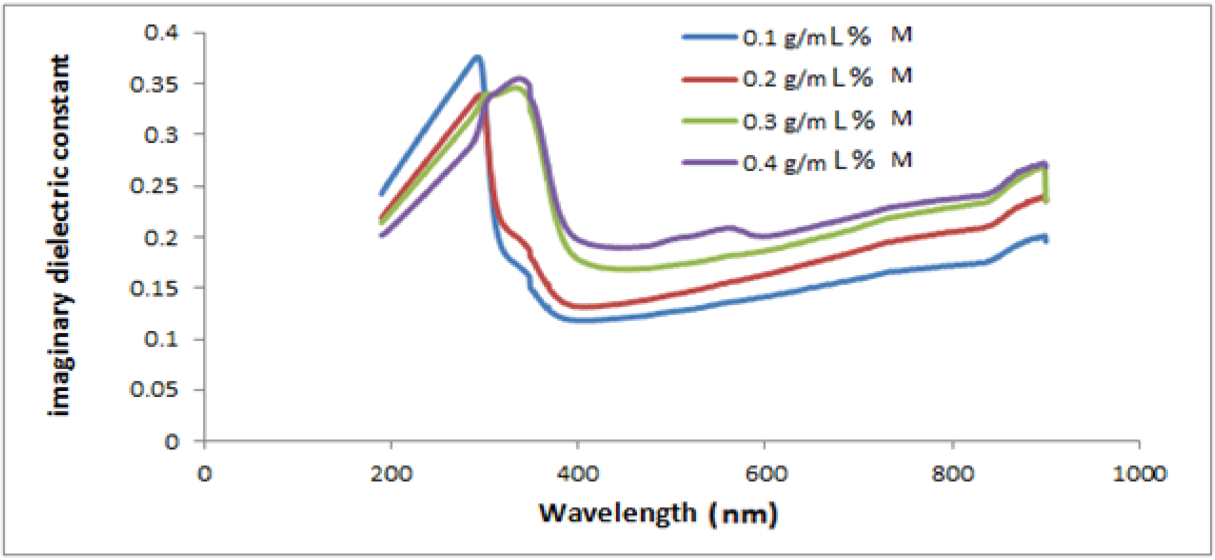


Figure (11) imaginary dielectric constant as a function of wavelength

Optical connectivity

As finding the optical connectivity of the relationship values (10) and the results of the optical conductivity as a function of the change in the wavelength of the light falling on polymer films illustrated in figure (12) found that the optical conductivity follow manner similar to the absorption coefficient and refractive index where the high value of the extent UV and decreased with increasing wavelength because it is an inverse relationship between the wavelength and energy of the optical conductivity increases with energy [30]

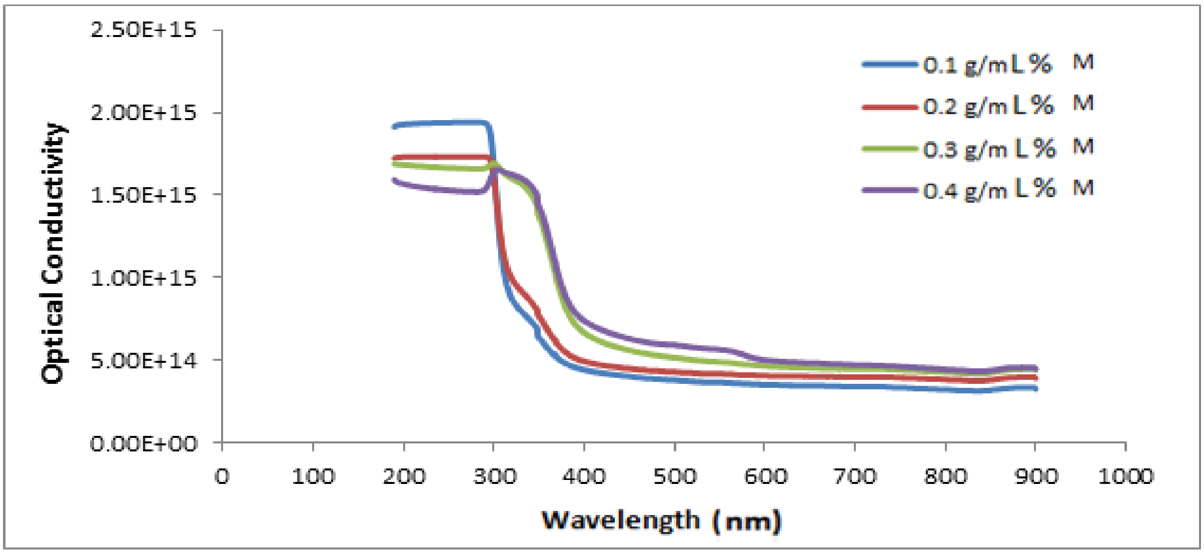


Figure (12) optical conductivity as a function of wavelength

CONCLUSIONS

1. The polymeric sulfides have been established to be useful basis.
2. The new semiconductor films prepared by drop casting method.
3. Properties are increased values with increased concentration except the transmittance, it decreases with increasing concentrations.
4. Properties are decreased values with wavelength values except the transmittance, it increases with increasing wavelength.

Experimental

General

Chemicals were purchased from Aldrich and Lancaster chemicals and mostly used without further purification. ^{1}H NMR spectra were recorded on a Bruker AV500 spectrometer operating at 500 MHz for ^{1}H. Chemical shifts δ are reported in parts per million (ppm) relative to TMS and coupling constants J are in Hz and have been rounded to the nearest whole number. Assignments of signals are based on integration values, coupling patterns and expected chemical shift values and have not been rigorously confirmed.

Typical experimental procedure for the preparation of 2,5-dimercapto-1,3,4-thiadiazole (1).

A mixture of (99%) hydrazine hydrate (5 mL, 0.02 mol) and carbon disulfide (15 ml, 0.02 mol) with dry pyridine (50 ml) was refluxed for (5 h). Then the excess solvent was then distilled off, and the resulting solid was separated out by adding (25 ml) of water and (5 ml) of hydrochloric acid. The mixture was then filtered and the solid was recrystalized from ethanol.

2,5-dimercapto-1, 3, 4-thiadiazole (1), Mp 164–166 °C ; IR (v, cm^{-1}): 1,624 (C=N), 3,200 (NH), 3,550 (SH);^{1}H-NMR (d-DMSO) δ (ppm): 9.85 (s, 1 H, NH).

Typical experimental procedure for the preparation of poly sulfides 1 and 2. Poly sulfide polymers 3 was synthesized by dissolving Na (0.84g, 0.035 mol) in 25 ml of absolute ethanol. Compound 2 (6.18 g, 0.017 mol) was added, and the solution was heated. To the resulting boiling solutions benzene was added (45 ml) and DCM (3.4 g, 0.017 mol). After the vigorous and spontaneous reaction subsided, 45 ml of benzene was added and the mixture was refluxed overnight. After mixture was cooled, it was filtered. The solution was evaporated under reduced pressure to give the corresponding polymeric sulfide 3 in 67% yield. Poly sulfide polymer (4; 70% yield) was synthesized by a similar procedure except using 1,6-dibromohexane (4.1 g, 0.017 mol) instead of 1,3-dibromopropane.

Poly sulfide 3. Yield 67%, Mp 246–248 °C; IR (v, cm^{-1}): 1,624 (C=N), 2,987-2,848 (C-H aliph.). ^1H-NMR ($CDCl_3$) δ (ppm): 3.10 (m, 4H, SCH_2), 8.10 (d, 4H, Ar-H), 8.50 (t, J = 7 Hz, 2 H, CH=N). Mn (GPC): 6519.

Poly sulfide 4. Yield 70%, Mp 267–269 °C; IR (v, cm^{-1}): 1,624 (C=N), 2,987-2,848 (C-H aliph.) ^1H-NMR ($CDCl_3$) δ (ppm): 1.50 (m, 4 H, $C\mathit{H_2}CH_2S$), 3.10 (t, *J* = 7 Hz, 4 H, CH_2S) 8.10 (d, 4H, Ar-H), 8.50 (t, J = 7 Hz, 2 H, CH=N). Mn (GPC): 6321.

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