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Synthesis of New Polymers Derived from Poly (Vinyl Chloride) and Study Their Optical Properties

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Abstract

Poly (vinyl chloride) (PVC) react with different amines in THF to form new polymers (PVC-L), which been characterize by spectroscopic methods. The structures of these complexes have been characterized by IR and Uv-Vis. Spectrophotometry. The optical properties of PVC in the region from (200-600 nm) were studied by preparing the composites PVC-L. The optical data analyzed and interpreted in term of the theory of phonon assisted direct electronic transition; it is observed that the energy is affected by doping type polymers used.

Keywords: PVC, optical properties, Energy gap.

Introduction

Synthesis of polymer-bound chelating ligands and the selective chelation of specific metal ions is a field of active research [1]. A number of ligands including polydentate amines, crown ethers, phosphines and bipyridines have been bound with mainly polystyrene divinylbenzene copolymers [2-3]. These studies are mostly concerned with ion-binding and catalytic aspects. Very little information appears to exist as to whether, and to what extent, such organic compounds can influence the properties of the macromolecule. Recently, scientists were able to modify PVC by introduction aromatic and heterocyclic moieties through halogen displacement reaction. PVC, thus modified, showed improved overall photochemical stability [4]. The facial chlorine displacement from PVC indicated the possibility on easy anchoring of ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes [5]. In recent years, studies on the electrical and optical properties of polymers have attracted much attention in view of their applications in optical devices with remarkable reflection, antireflection, interference and polarisation properties [6-8]. The optical properties of polymers can be suitably modified by the addition of dopants depending on their reactivity with the host matrix. The amines polymer are fast-conducting complexes in a number of crystalline and amorphous materials, its incorporation in a polymeric system may be expected to enhance its electrical and optical performance. In this paper, we present results of such a study on the optical properties of pure and other polymers PVC films.

Experimental

Materials and Methods

Synthesis of PVC –Ligands compounds [9] (0.1 g) of PVC was dissolved in dry THF (20 ml), then add (0.05 mole) from appropriate amine. The reaction mixture was heated under reflux for (2-6)h. The hot mixture was transfared to pitredish, the precipitate modified polymer separated as film by evaporated the solvent . The color prepared polymer and time of reflux are found in Table (1).

Table (1).

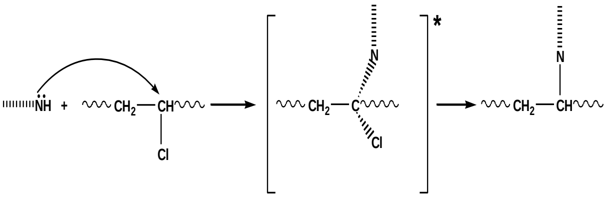
Amine (Ligand)	*Time reflux (h)*	*Color of PVC - Ligand*
2 – amino thiazole	3	Brown
2 – amino imidazole	3	Brown
2 – amino pyrimidne	3	Yellow
4 – nitroaniline	6	Yellow
2,5 –dichloroaniline	6	Yellow

Films Preparation:

0.5% concentrations of PVC solution in THF was used to prepare 30 micrometer thickness of polymer films, (measured by a micrometer type 2610 A, Germany). The films were prepared by evaporation technique at room temperature for 24 h. To remove the possible residual tetrahydrofuran solvent, film samples were further dried at room temperature for three hours under reduced pressure. The optical absorbance (A) of the sample was measured as a function of wavelength (λ) ranged from 200 to 600 nm by using computerized Shimadzu Uv-vis 160A-Ultraviolet-spectrophotometer full-scale absorbance up to (2.5). The light sources are halogen lamp and socket-deuterium lamp. The detector is Si-photodiode and all measurements were performed at room temperature. UV/VIS absorption spectroscopies were made for prepared samples before and after conjunction. The spectra were used to carry out the energy gap by plotting $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ with (r) value (1/2) which indicates a transition of direct type. The linear portion was best fitted with (r=1/2) Energy gap shift for all samples plotted as a function to conjunction type [10].

Results and Discussion

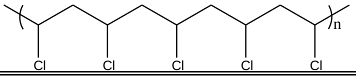
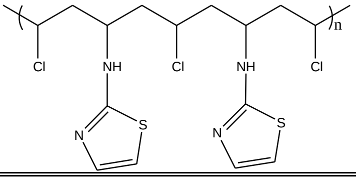
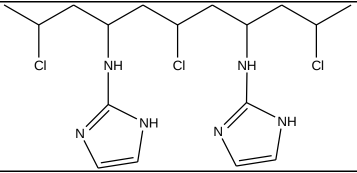
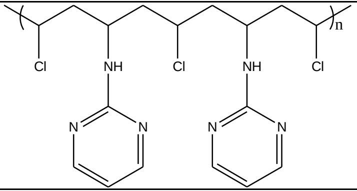
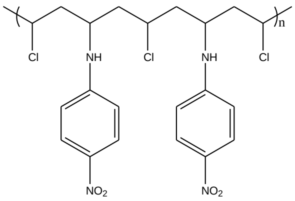
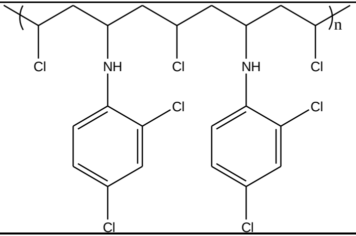
The reaction was initiated by the nucleophilic attach of (N) atom on the carbon carrying chlorine atom in the polymeric chain followed by departure of chloride anion as a good leaving group.



The structure of the modified polymers was established on the basis of its FTIR and UV-Vis spectroscopy, each of the present polymers showed other bands characteristic of its own structure.

The successful modification of PVC with different amines can be demonstrated by FTIR spectroscopy. absence of obsorption bands due to ($-NH_2$) stretching frequencies of amines, clearly inidicated the reaction between PVC and amines These compounds clearly revealed the three characterstic vibrations of the C=N, N-H. The most common bands are tabulated in Table (2). The ultraviolet-visible spectrophotometry technique is use to characterize the prepared polymers in (THF) as a solvent. The ultraviolet visible electronic spectra of the prepared compounds and modified polymers showed an absorption bands could be attributed to the $\pi \rightarrow \pi^*$ electronic transitions, these transitions are assigned in relevance to the structures of compounds and polymers. As shown in Table (2). The increase of the absorbance in the Uv-Vis range for samples containing prepared compounds or modified PVC compared with (PVC) can be explained by the formation of conjugation double bonds (band corresponding to the $\pi \rightarrow \pi^*$ transition) in these modified polymers resulting from introducing an aromatic rings. Thus, shifting the absorbance to longer wavelengths (i.e the bathochromic effect) is good evidence that modification were formed in our PVC and compounds. Moreover, the broading in the bands caused by the presence of other chromophores such as (NO_2, etc) which absorb in the above region and this overlapping bands make the interpretation of the results difficult. On the basis of the preceding discussion, the structure of the complexes suggested as shown in Table (2).

Table (2)
Characteristic absorption bands of Modified polymers, Electronic spectra and suggested structure.

Compound	*IR (cm^{-1})*	*Assignments*	*Absorption Bands (nm.)*	*Suggested Structure*
PVC	2910 612	C-H C-Cl	269	
P1	3210 3190 2916 – 852 1604 1045	N-H (-C=C-H) C-H aliphatic C=N , (C=C) C-S	273, 265	
P2	3274 3060 broad 2916 1637 632	N-H C-H (aromatic) , (C-H) alken C-H (aliphatic) C=N (endocyclic)(C=C) C-Cl	276	
P3	3300 3069 2918 1645 609	N-H (-C=C-H) C-H (aliphatic) C=N , (C=C) C-Cl	283	
P4	3224 2100 2918 1650 1596 1320 839 692	N-H C-H (aromatic) C-H (aliphatic) N-H (bending) Asym.NO_2(N-O) Sym.NO_2 (N-O) P-disubstituted C-Cl	283	
P5	3400 3090 2914 842 754 613	N-H C-H (aromatic) C-H (aliphatic) P-disabshtuted benzene ring O- disabstituted benzene ring C-Cl	252	

The relation between $(\alpha h\upsilon)^2$ versus photon energy for the PVC samples are shown in Fig.(1 to 5) for allowed transition. For polymer samples shown in Figs. (1 to 4), the shift in the energy gap could be attributed to the formation of polorans in the films. The evidence of Polaron formation is made that the reaction in band to band transition due to shifting the band density of state toward the energy gap. This observation is not similar to the doping in conventional semiconductors when the band to band absorption strength does not affected by the formation of dopant state in the energy gap. The effect of the organic addition on the values of phonon energies is also investigated and the results are shown in Table (3). The results presented in Figs. (1 to 5) indicate the existence of two polaron bands in the energy gap. The first one represents the transition from valance band to bonding polaron band. The second band represents the transition from valance band to anti-bonding polaron band, which is in a good agreement with results, are obtained by [4-7]. The Energy gaps were measured as behavior of a conductivity measurement of PVC with and without additive can obtain by adopting the data of energy gap, (see Table (3) and Figs. from (1 to

5)). The conductivity measurement for PVC in the presence of additive increase in the following order. PVC, P1, P2, P3, P4, P5.

Table (3)
Indicate the energy band gap according to the direct allowed transition.

Polymer	***Eg (eV)***
P1	2.41
P2	2.91
P3	3.71
P4	3.73
P5	3.75
PVC	5.20

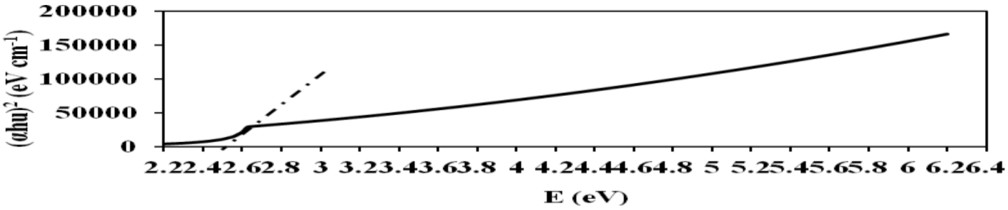


Fig. (1) Allowed direct transition (αhv)2 Vs. Energy for the sample P1.

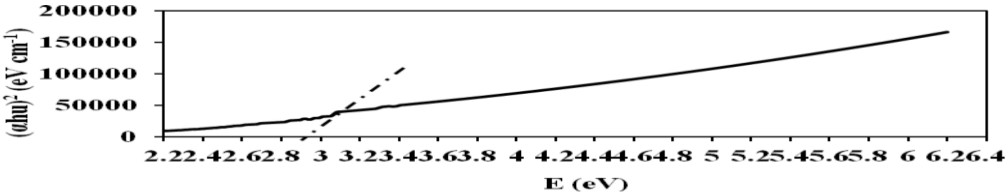


Fig.(2) Allowed direct transition $(\alpha hv)^2$ Vs. Energy for the sample P2.

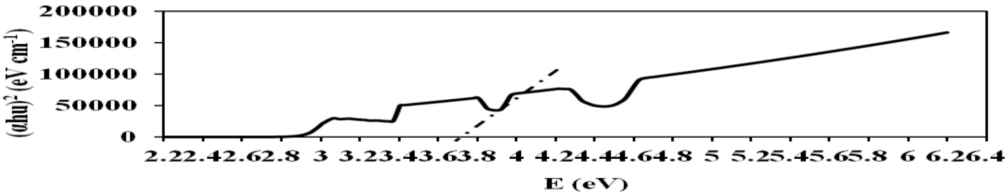


Fig. (3) Allowed direct transition $(\alpha hv)^2$ Vs. Energy for the sample P3.

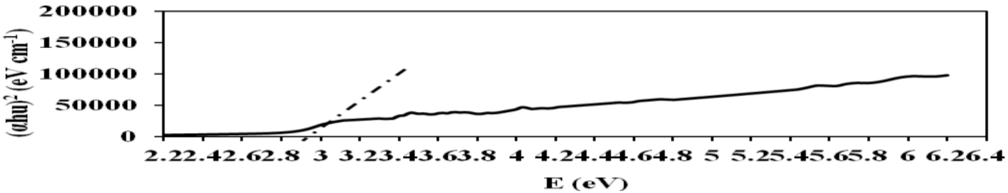


Fig.(4) Allowed direct transition $(\alpha hv)^2$ Vs. Energy for the sample P4.

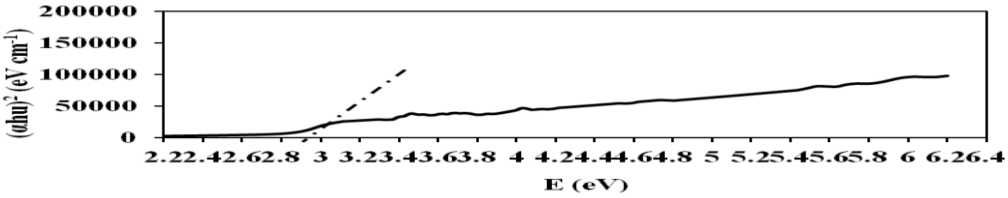


Fig. (5) Allowed direct transition $(\alpha hv)^2$ Vs. Energy for the sample P5.

Conclusion

The optical absorption in the UV-visible region for PVC polymer with different amines. The Energy gaps were measured as behavior of conductivity and it is conceded that the energy is affected by type of polymer prepared.

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الخلاصة

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القياسات البصريه للبوليمرات تم قياسها في المنطقه المحدده بين 200 الى 600 نانوميتر ومن خلال حساب فجوه الطاقه استتنجنا توصيليه البوليمرات الجديده.