Chapter I

Introduction

Introduction

I-1. General Introduction:

The sunlight received by a surface on earth can be divided into three different types (1): direct, diffuse and reflected. Diffuse sunlight approaches a surface from all unobstructed angles, while direct-beam rays strike the surface from only one angle. In addition to diffuse and direct light, an angled surface can also received reflected light from the ground or other appropriately positioned surfaces.

There is some mechanism for the interaction between the absorbed light and the nuclear, molecular or electronic changes occurring in materials. There must be some electric or magnetic effect produced by the change which can be influenced by the electronic or magnetic fields associated with the radiation. Photoconduction is one of nonequilibrium process that occurs in interaction of light with solid materials. It consists in the appearance of a change in the conductivity of a semiconductor under the effect of some radiation (infrared, visible or ultraviolet).

The electrical conductivity in solids is very important property to differentiate between various types of solids. It encompasses a wide range of values, which characterize: insulators, semiconductors and metallic materials. The mechanism of electrical conduction can be explained by many models (2). According to band theory, if the valence bands, which contain electrons, are completely filled while the conduction bands are empty the materials is considered as insulators and show a very poor conduction. If, on the other hand, the highest-lying occupied band contains large fractions of both occupied and empty states, the solid behaves as a metal and shows a good conduction. But if this highest occupied band contains only small concentration of occupied or empty states the materials behave as semiconductor and show an intermediate conductivity. There are, however, many differences in the electrical properties of these different types of materials. The most important of these is the effect of temperature on the electrical conductivity. As a general rule the electrical conductivity of metals decreases with increasing the temperature, while the conductivity of the semiconductors and insulators show a reverse temperature effect due to the nature and behaviour of charge carriers in these materials.

Generally, it can be said that the conductivity depends on the concentration of charge carriers and their mobility. In metals, electrons are the main charge carriers and move throughout freely, they are not localized or bound atomic sites. There is therefore essentially no activation energy required for the conduction process. The number of mobile electrons is large and essentially constant, but their mobility gradually decreases with rising temperature due to electron-phonon collisions. Consequently, conductivity gradually drops with rising temperature. In semiconductors, the number of mobile electrons is usually small. This number may be increased in one of two ways, either by raising the temperature so as promotes more electrons from the valence band to the conduction band, or by doping with impurities or substances such as dye on polymer that provide either electrons or positive holes. In the first of these, the charge carriers and the conductivity rise exponentially with temperature (intrinsic semiconductivity), the relatively small change in mobility with temperature are completely swamped by the much large changes in concentration. In the second of these, extra mobile carriers are generated by the addition of dopants at low temperature (extrinsic conductivity). The concentration of these extra mobile carriers is much greater than the thermally generated intrinsic carrier concentration. Consequently, concentration is independent on temperature and conductivity shows a slight decrease with temperature due to mobility effect mentioned above. In insulators, however, electrons are not free to move throughout the bulk of materials but are bound to atomic sites. They differ from semiconductors only in the magnitude of their conductivity, which are usually several orders of magnitude lower. Thus, the conductivity of insulators is also sensitive to both temperature and dopants.

Semiconductor with only a few electrons in the highest occupied doped level called n-type and those with only a few empties, or holes, are called p-type (2).

Polymers are almost always good insulators and it is difficult to observe any electronic conductivity at all. Their conductivity depends usually on the movement of adventitious ions (3). Consequently, any improvements in the quality of insulation are generally won by careful preparation and purification, so as to avoid as much as possible the presence of ionic impurities, including catalyst residues, products of oxidation and dissociable end groups. Although low conductivity is the normal for mist polymers, special high-conductivity polymers, based on certain organic molecular structures which are known to exhibit electronic conductivity have been made. The major practical solution to the problem, where only a moderest level of conductivity is required, is to make a conducting composite material by dispersing a conductive element, like a metal or carbon, in an insulating polymer. Generally, The basic insulating properties of polymers are more than adequate for many purposes, and any development effort may then be primarily concentrated on improving other aspects of the material's performance.

The world energy crisis has given a new impetus to the solar energy utilization research and development program all over the world. Terrestrial solar radiation is a low-intensity, variable energy source arriving at about 1000 W/m^2. The economic feasibility of solar energy utilization depends upon efficient collection, conversion and storage (4). The efficient utilization of solar energy for heating, cooling and process applications requires the use of flat-plate or focused collector systems which first capture as much as possible of incoming radiation and then deliver a high fraction of the captured energy to the user which is generally a working fluid. The conversion efficiency of a collector system is limited by the thermal losses from the heated absorber due to conduction, convection and radiation. The economical and efficient utilization of thermal energy derived from solar radiation using solar collectors requires an efficient and low cost solar "selective surface".

Solar energy can contribute considerably to solve the energy problems if appropriate methods were developed to collect, concentrate and convert solar radiation. Two main approaches must be pursued to decrease the cost of solar electric energy. The first is to reduce the cost of solar cells whose production is still very expensive (5) so that producing low-cost devices, solar energy conversion by photoelectrochemical (PEC) cells ("wet solar cells") have been intensively investigated (6,7). In 1873, Herman Vogel (8) discovered that certain organic dyes could extend the green and red response of silver halide photographic films. The mechanism was later found to involve the electron or energy transfer from the organic chromophore to the semiconducting silver halide grain. This spectra sensitization, as it has come to be known is the basis for modern photography. Photovoltaic cells have also been known for quite some time. Modern solar cells, on the other hand, are a more recent development, the first being developed in 1954 at RCA by Paul Rappaort and Bell Labs by D. Chapin and G. Pearson (9). These cells employed a solid state or p-n junction which marks the barrier between regions of electron and hole conduction. Electrons and holes created via the absorption of light in silicon wafer diffuse at different rates in the n-doped and p-doped materials are eventually collected at the junction. This p-n junction is formed by a process which resembles that used by the semiconductor industry to manufacture integrated circuits and computer chips. Potentially more coast effective technologies, which use thin films of such materials as amorphous silicon deposited on glass, are under development (10). Although the equivalent of 50-60 MW of solar cells are currently produced each year (10), no technology has produced commercially available, efficient, reliable and low coast modules that can be used on the exterior of buildings.

Using sensitization process in solar cells has also been explored. Early work was done by researchers such as Tributsch et. al. (11). Recently, Greatzel research group has combined several concepts to produce low cost 7% efficient solar cells (12,13). The cell, which is called a nanocrystalline dye sensitized solar cell, is remarkable in that it resembles natural photosynthesis in two respects: (1) it uses an organic dye to absorb light and transduce solar energy and (2) it uses multiple layers to improve the absorption and collection efficiency over that of thicker layers. It is one of a new class of devices which are called molecular electronic devices (14). To create the cell, a water solution of nanometer size particles of TiO_2 is deposited directly on conductive glass by a process similar to that of painting (15). The use of TiO_2 in photovoltaic cell has many advantage: it is cheap, abundant, nontoxic, biocompatible and is widely used in paints and care products.

The second approach used to decrease the cost of solar electric energy is that to concentrate the light as much as possible on a small area. Common methods of concentrating light are mirrors or lenses which are limited in that they require direct sunlight and direct tracking of the sun. So that the luminescent solar collectors (LSC) have been proposed for solar energy conversion into electrical energy. Weber and Lambe (16) were first to suggest the principle of operating of LSC. The operating of LSC is based on the principle of light trapping by total internal reflection. Transparent materials like PMMA and inorganic glasses having high refractive indices are doped with efficient luminescent molecules or ions having strong absorption bands in the region (400 – 700 nm). Solar radiation is absorbed and re-emitted as luminescence, a large fraction (~ 75% for PMMA having an index of refraction of 1.49) of which is trapped inside the collector medium due to total internal reflection. After a number of reflections the luminescence radiation reaches the edge of the plate where a suitable photovoltaic cell converts it into electrical energy. The chief advantage of LSC is that the cost of electrical conversion can be reduced provided a viable system comes up which, however, is still far from realization in practice.

One of the important problem in the development of LSC is to find an activator which absorbs strongly in the most intensive part of solar radiation lying in the region (400 – 900 nm) and convert the absorbed energy into luminescence with maximum possible efficiency (17). It is desired that the luminescence matches the spectra region of sensitivity of photovoltaic cell used. Thus, the relatively low efficiency of solar cells exposed to white light can be circumvented by coupling a LSC to an appropriate photovoltaic cell and hence solar spectrum can be used more efficiently. The other requirements of activator used in LSC are: (a) separation of absorption from emission band in order to reduce self-absorption (b) good photochemical stability.

Organic dyes are considered good luminescencent materials for LSC purpose, because these have large absorption over a wide spectrum range and higher quantum efficiencies than inorganic materials. PMMA is a good matrix for LSC (highly transparent and high refractive index), on the other hand it is easy to prepare as a sheet of desired shape and size. LSC have the following advantages over conventional solar collectors (18):

(1) They collect and concentrate both direct and diffuse light.

(2) There is good heat dissipation of non utilized energy by the large area of the collector plate in contact with air so that "cold light" reaches the solar cells.

(3) Tracking the sun is unnecessary.

(4) The luminescent species can be chosen to allow matching of the concentrated light to the maximum sensitivity of the photovoltaic cell (19,20).

I-2. Literature Survey:

The electrical conductivity of pure and mixed PMMA with different dyes, at different conditions of temperatures, frequencies of electric field, irradiation, pressure....etc., have been investigated (21-25).

El-Shahawy (21) studied the AC-conductivity for PMMA solid samples free and mixed with coumarin-6 and fluorecein sodium organic laser dyes at different frequencies and temperatures. The conductivity was found to be attributed to an electronic hopping transport at charged defect sites (dangling bonds) accompanied by orientational polarization at higher temperatures. The correlated barrier hopping (CBH) mechanism was found to be the most appropriate model from which the density of localized states were deduced. The fluorecein sodium dye mixed sample showed the highest concentration of charged defects and at the same time, suffers the highest potential barrier. And it was found that the electrical conduction for a coumarin dye mixed sample is dominated by its plastication effect due to an enhanced free volume. Conversely, for the fluorecein sodium dye mixed sample, intermolecular interaction between the solute and dye molecules seems to be the more effective factor.

Khare et. al.(22) investigated the electrical transport behaviour of ferrocen mixed polymethylmethacrlate (PMMA) films, which is deposited by isothermal immersion technique in the temperature range of 333 - 373 K and electric field from (2.0-4.0) x 10^4 Volt/cm. They found that at higher fields and temperatures, the observed conduction behaviour could be described by the Richardson-Schottky emission. The increase in current due to doping was explained on the basis of the formation of charge transfer complexes where the dopant molecules act as an additional trapping center and provide a link between polymer molecules in amorphous region.

Electrical conductivity was also studied for pure and doped PMMA films with TCNQ-anthracene. The effect of concentration of the dopant, temperature and light on the electrical behaviour of these films was investigated (23). The sensitivity of the PMMA doped films for photoconductivity is discussed on the basis of the conduction mechanism proposed for the charge transfer interaction in the complex systems.

The AC-conductivity of two acrylate groups namely, polymethymethacrylate and polyethylmethacrylate have been evaluated (24) in the frequency range of $10^2 - 10^5$ Hz and the temperature regions of 311 – 337 K and 89 – 114 K. The results showed that the AC-conductivity σ_{AC} obey the relation $\sigma = A\ \omega^s$ where s lies between 0.86 to 1.0 and this agreement with the results obtained for amorphous solids.

The effect of light and the change in thickness on the electrical conduction of pure and doped PMMA was also investigated by **Sawaby** et. al. (25). They found that the resistivity of PMMA decreases gradually with increasing exposure time and the effect was found to be reversible. The doped samples showed more stability against the light effect and the current-voltage (I-V) characteristics indicated that the mechanism of conduction of PMMA depends on the presence of localized states or trapping levels arising from lack of order.

Dielectric constant (ε`) and dielectric loss (ε``) for solid samples of PMMA free and mixed with coumarin-6 and fluorescein sodium organic laser dyes have been studied as a function of temperature and frequency by **EL-Shahawy** (26). It was found that both dyes have an increasing effect on both the magnitude and the rate of the increase in ε` with temperature. For pure PMMA, two regions were obtained which were assigned to β process at lower temperatures and αβ process one at higher temperatures with activation energy values of 16.1 and 21.6 kcal/mol respectively. On the other hand, in fluoresein sodium dye-doped sample, the presence of the dye hinders the α process of the host polymer due to intermolecular interactions between the polymer molecules and the solute dye. Coumarin-6 dye-doped sample exhibited an entirely plastification effect as reflected in the lower values of the temperature of ε''_{max}.

Mudarra et. al. studied (27) the effect of the polarization time in the formation of the PMMA space charge relaxation. The study has been carried out by thermal stimulated depolarization currents of electrets formed by windowing polarization. The results obtained have been fitted to the general kinetic order model, and they are consistent with the existence of a space-charge polarization mechanism with the kinetic order of 1.14. The intensity of the peak maximum results in being a good indicator of the trapped carrier number evolution. For high temperatures and high electrical fields the saturation of this mechanism is achieved faster, which is attributed to the increase in the mobility of the charge with these variables.

The relaxation of cast PMMA films have been studied by dielectric spectroscopy (28), where conventional PMMA was dissolved in various solvents (chloroform, toluene, tetrahydrofuran and acetone) and the solutions obtained were then casted on a substrate. The influence of the nature of the solvent on the relaxation temperature of PMMA and the variation of the loss factor (tanδ) with temperature were analyzed. The results showed that the tan δ peak corresponding to the α-transition (glass transition) is shifted towards lower temperatures, compared with that of the bulk polymer. The temperature of β-relaxation is decreased for chloroform and increased for other solvents. The results were explained based on acid-base interaction between PMMA and trapped solvent molecules.

The organic laser dyes K1, Rh.6G and Rh.B have been used as the dopant species in PMMA as the matrix material to study the effect of structure and sample preparation on the dielectric characteristics of LSCs (29). The temperature dependence of dielectric permittivity (ε`), dielectric loss (ε``) and AC-conductivity (σ_{AC}) have been carried out for the pure and dye doped samples at 1, 10 and 100 kHz. The effect of dye concentration on these parameters for Rh.6G samples prepared by a precast method were discussed in terms of an offered free volume enhancement of polarization at low dye concentration, together with the contribution of dye molecules at higher ones. On the other hand, the effect of dye addition is found to be strongly dependent on sample preparation. Among the dye-doped samples prepared the K1-doped one showed lowest temperature gradient permittivity and highest thermal stability.

The effect of photodegradation using UV radiation on β-relaxation in PMMA was investigated (30) dielectrically within the temperature range 333 – 363 K and 20 – 10^5 Hz frequencies band. It was found that the irradiation samples exhibit a β-relaxation process similar to that of unirradiated PMMA but with broader distribution of the relaxation times. Increasing the time of UV exposure increased the time of the relaxation and displaced the peak toward lower temperature and decreased the activation energy with irradiation.

Relaxation dynamic of PMMA and doped PMMA systems were investigated as a function of processing temperature and frequency (31). The results showed that polymer relaxation and the changes in local mobility are responsible for chromophore reorientation and lead to a loss in second-order nonlinear optical (NLO) properties.

El-Shafee studied (32) the dielectric behaviour of solution-grown thin films of PMMA containing p-nitroaniline as a dopant within temperature range 333 – 363 K and a 20 – 10^5 Hz frequency band. It was found that these mixtures exhibit only one relaxation process similar to that of pure PMMA. However, the addition of p-nitroaniline increased both the height and the relaxation strength and also the additive causes narrowing of the loss curves and increase the activation energy for relaxation. These results were interpreted in terms of the hydrogen bonding effects of p-nitroaniline on localized motion of carboxymethyl dipoles in PMMA.

The dielectric properties of solid solutions of p-nitroaniline in poly(methylmethacrylate), poly(ethylmethacrylate) and poly(n-butylmethacrylate), were investigated in the frequency range from 20 to 10^6 Hz (33). The results showed that the solute has a strong influence on the relaxation process of PMMA, and this ascribed to the formation of hydrogen bond between the amino group of the solute and the side groups of the polymer. In poly(ethylmethacrylate) this effect was found to be less pronounced and it is absent in the case of poly(n-butylmethacrylate). This suggests that the increasing in the size of the n-alkyl group prevent hydrogen bond formation between solute and the polymer.

The effect of small amounts of admixtures in PMMA on dielectrical relaxation processes over the region of 200 – 350 K, which is conventional considered to be the region of dipole polarization of macromolecules, was investigated by **Bubman** et. al. (34). The mechanism of relaxation polarization is related to the formation of charge-transfer complex in the polymer, containing the molecules, which can accept admixtures.

Gomez et. al. studied (35) the effect of physical ageing on the dielectric behaviour of PMMA at several temperatures and at frequencies in a range from 0.2 - 100 kHz. Measurements of the more prominent relaxation (β-relaxation) reveal structural recovery although the effects are not so striking as in the measurements by dynamic mechanical methods and the coupling molecular model has been used to account for the experimental results.

The optical and dielectric properties of prepared polyvinylchloride/atactic polymethylmethacrylate blends were studied as a function of applied field frequency and PMMA content (36). The optical energy gaps and the energy gap tails were determined. It was found that the applied frequency and the PMMA concentration have some effects on the physical parameters such as the optical energy gap, the glass transition temperature (T_g), the dielectric constant and the refractive index. The observed changes in these physical parameters are due to structure changes in the amorphous domain, impurities and space charge within the interface in the mixed phases.

The effective optical gain was investigated in a PMMA plastic slab doped with perlimide dyes and found that to be positive (37). The experimental set-up is based on a single exciting laser beam, and the detection of a one pass amplified light emitted along the length of an optically exited sample. It was found that the photoluminescence output intensity varies exponentially with the length of the excited region and under moderate pumping intensities, net laser gains of 53 and 36 cm^{-1} are measured for yellow KF 241 and red BASF 339, respectively.

1,1,4,4-tetraphenyl-1,3-butadiene, coumarin-334 and rhodamine 6G have been used to form single, binary and ternary dye-doped PMMA thin films by the dip-coating method (38). The thickness of the films was controlled by adjusting the polymer concentration. The photophysical properties of the dyes in solution and in film have been investigated by steady-state and time-resolved fluorescence spectroscopy. Excited-state resonance energy transfer between these dyes has been observed leading to a very broad color emission by the ternary system when excited with ultraviolet light. Laser excited led to radiation enhancement by wave guide gain and to extensive spectra narrowing.

The effect of the addition of polymer liquid crystals as dispersed molecules to PMMA on the optical properties in the UV-visible and near infrared region was investigated (39). From transmission, absorption and reflection spectra the absorption coefficient $\alpha(\omega)$ and refractive index (n) as a function of angular frequency of radiation (ω) have been calculated at room temperature. The values of the optical band gap (E_{opt}) and the band gap (ΔE) were also evaluated. Both the parameters (E_{opt}) and (ΔE) were found to be varied with the mixing ratio of dispersed liquid crystals.

The emission spectra of irradiated and non-irradiated thin films of PMMA matrices containing rhodamine B (RhB) or rhodamine 6G (Rh6G) as donors and chloranil (CA) as acceptor, have been studied by **El-Agramy** et. al.(40). The results showed a single radiophotoluminescence peak at 570 nm and the maximum fluorescence intensity at a doping concentration ratio of 6 : 4 acceptor to donor. The Rh6G-CA is sensitive to UV light and re-emitting in the visible region and hence, could be used as a luminescent concentrator for solar cells.

Bakr et. al. (41) studied luminescent solar concentrator, which was prepared using a bulk sheet from PMMA doped with different luminescent dyes (K1, K27 and Lpero) during polymerization process. The results showed that photo-and thermal-stability of the Lpero dye system is the most stable one.

A single luminescent solar concentrator (LSC) has been prepared by **Salem** et. al.(42) using oxazine 750 dye and PMMA, dissolved in benzene. The solar simulation of the LSC has been performed at four different positions using an X-Y tracker. The hourly output power and global solar radiation has also been measured for a full year from April 1995 to March 1996, considering day 21 as a reference day. The output power curves were studied for each month separately and averaged through four seasons, Summer, Autumn, Winter and Spring. The optical efficiency was also calculated and discussed.

Three luminescent solar concentrator (LSCs) samples have been prepared using BASF-241, 402 and 339 dyes dissolved in methymethacrylate (MMA) and thermally polarized (43). The optical efficiencies of these samples were measured and calculated hourly through the year (1996 - 7) considering day 22 as the reference day for each month. The optical absorption measurements have been carried out at room temperature before and after the samples were exposed to daylight. The optical absorption edges were analyzed and the photostability of the samples tested.

The optical efficient of some liquid concentrators has been studied by **Mansour** (44). It was found that the liquid concentrators are as efficient as those with solid matrices and their efficiencies are enhanced under diffuse light illumination. A single dye luminescent solar concentrator has been prepared using BASF-241 and 402 dye dissolved in methylmethacrylate and thermally polymerized. The optical efficiencies were measured and calculated hourly for one season (summer 1996) considering day 22 as a reference day foe each month. The performance of LSC has been tested at four different positions.

Pretre et. al. (45) established methods for determining the real and the imaginary parts of the index of refraction and the second hyperpolarizability as a function of wavelength for a composite polymer, for either a guest-host or a side-chain system. The methods allow for an accuracy in index of 3%, if the wavelength range includes the main absorption band of the chromophore of 0.2% for wavelengths 400 nm and more to the long-wavelength side of λ_{max}.

Luminescent solar concentrator (LSC) samples with PMMA as the matrix were prepared by a casting method using the organic laser dyes: Rh.6G, Rh.B and K1 (46). Optical absorption measurements have been carried out in the wavelength region 200 – 900 nm at room temperature before and after the samples have been exposed to sun light for up to 95 days. The obtained spectra in the visible region are interpreted in terms of photodegradation of the dye molecules. On the other hand, the UV-spectra and the optical absorption edge were analyzed in the light of approaches delivered by Urbach and by Davis and Mott.

Absorption and emission spectroscopic techniques were applied (47) to study some dye molecules: fluorescein, eosine, erythrosine, rhodamine B, rhodamine 6G and acridine orange alone and in solution (polyethylene glycol 400, 600 and 700) in order to establish the changes in photostability of these dyes, which could be used for fluorescent solar concentrators.

Absorption spectra, emission spectra and quantum efficiency for PMMA doped with oracent 6 GF at different concentrations were investigated by **Grigorescu** et. al. (48). Fluorescent characteristics allow determination of dye optimum concentration and of concentrator efficiency.

Pandey et. al.(17) suggested the preparation of luminescent solar energy concentrators based on uranyl-ion-doped in polymethylmethacrylate (PMMA). A qualitative study showed that alkaline species of uranyl ion with high fluorescence intensity can be a good activator for LSC.

Spectral characteristics of some luminescent dyes, derivatives of xanthene and benzoxazinone groups, in a liquid polymer matrix, Triton x-100 have been studied (49). It was seen that Triton x-100 could serve as a suitable liquid matrix for the luminescent solar concentrators.

Optical efficiencies for luminescent solar concentrators based on thin films of PMMA doped with luminescent dye BASF-241 deposited on PMMA transparent plate were investigated by **Eyal** et. al.(18). The influence of the refractive index of optical matching material on LSC performance was analyzed.

A benzoxainone derivative, DFSBO (7-dimethylamino-3-(p-formyl-stryryl)-1,4-benzoxazine-2-one) was compared to DCM and Rhodamine 640 for applications in luminescent solar concentrators. Plates made of PMMA doped with these dyes were investigated regarding spectra characteristics, gain in current intensity of the photovoltaic cell, concentration factor in terms of power and photochemical stability (50). It was found that among the three dyes investigated DFSBO the best performance.

Luminescent solar concentrators containing uranyl ion were investigated by **Folcher** et. al. (51). The results showed that fluorescence quantum yield of 0.7 was measured at low uranyl concentration (less than 1%) and decreased when the concentration increased. This variation was correlated with the life time of the excited state and was due to uranium-uranium interactions, where these quantitative determination can be used to optimize the thickness of the concentrator sheet.

The principle of a luminescent solar concentrator was analyzed with an emphasis on the photon-transport yield. A mathematical model is developed, which takes into account the loss factors related to the photon transport in the LSC matrix (52). The relations obtained show that whereas the optical efficiency is still a decreasing factor with the LSC size, the concentration ratio can be optimized with regard to the geometry, the input surface and the thickness of the LSC. The experimental analysis, carried out on two types of fluorescent PMMA, confirm the effects of these geometrical parameter on the LSC performances. A concentration ratio of 22 has been obtained experimentally with monochromatic irradiation and a flux gain of 9.5 has also been determined in real conditions.

The spectra characteristics of 18 organic laser were studied for their applicability as luminescent centers. The spectra homogeneity and self-absorption characteristics of representative dyes were examined (53). Three independent techniques for measuring self-absorption rates were used. These are time-resolved emission, steady state polarization anisotropy and spectral convolution. It was found that the performance of LSC which achieved high light concentration is primarily limited by self-absorption and by photodegradation. The maximum efficiency possible is about 9% in such systems and present devices can achieved about 3%. A typical lifetime for an LSC using organic laser dyes due to photodegradation is on the order of a month.

An indoor test stand for fluorescent planar concentrator-collectors (FPC) with a 1.6 kW xenon light source, irradiating a rectangular triangle (active area 400 cm^2) with 82 m W cm^{-2} and a typical homogeneity of ± 10% was described (54). Conditions and definitions for the efficiency measurements were also discussed, taking into account intensity and reflection effects. The influence of thickness variation and enhancement in solar cell efficiency were discussed. It was found that the best optical efficiency was 7.5% for a single-plat one-dye FPC.

Techniques and calculations were presented by examine a single dye (or inorganic ion) LSC with emphasis on the planar geometry (55). They give explicit expression for the over-all performance of a luminescent solar concentrator in terms of the intrinsic spectra response and quantum efficiency of its constituents.

Experiments were described illustrating enhanced photon trapping and efficient energy transfer in mixed-dye planar solar concentrators containing, Rhodamine 6G and Coumarin 6 (56). These concentrators intercept more of the solar spectrum to give an enhanced photon-flux gain that exceed the single-dye concentrator. It was also shown that the energy absorbed by the donor dye is transferred efficiently into the emitting acceptor by two competing processes.

Taleb (57) studied the effect of self absorption accompanying most dyes used as a luminescent solar concentrators in the form of rigid sheets, allowing for more efficient solar concentrators and hence high photovoltic solar conversion. The treatment involved mixing dopant molecules of specific properties with the dyes before forming the rigid final shape. Dyes including Rhodamine 6G, Rhodamine B, Ruthenium bi byridyl and crystal violet were used while thionin molecules were utilized as the dopant. The study showed that the efficiency enhancement is a function of dopant concentration and sample thickness.

Many authors used titanium dioxide which possess a large band gap energy (3.2 eV) for anatase phase in preparing dye sensitized solar cells (58-69).

Harizanov et. al.(58) showed a technological approach for the processing of stabilized xerogel colloidal titanium oxide films, where glycerol was used as a drying control additive agent and helped in stabilizing the solution. The thermal transformation of xerogel was studied by differenational thermal analysis (DTA) and powder X-ray diffraction. The optical index of the annealed coating was evaluated using UV-VIS-NIR spectrophotometry. The results showed that a nanocrystalline titania anatase film of high optical quality ($n = 2.34$ at 600 nm) can be obtained by the sol-gel process.

The binding of the common ligand bi-isonicotinic acid (4,4`-dicarboxy-2,2`-bipyridine) to TiO_2-antatase (1 0 1) surface by means of quantum chemical calculations was studied by **Persson** et. al.(59). Different adsorption models were studied with carboxyl oxygen binding to surface Ti-atom, and the acidic protons bonded to surface oxygens. A moderately deformed surface-binding ligand with two 2 M-bidentate (bridge) dye-surface bonds was found to be more favourable than both the currently prevailing dye-sensitization model of an undeformed 1 M-monndentate (ester) binding adsorbate structure, and a 1 M-bidentate surface-binding adsorbate structure.

The application of light scattering of submicron TiO_2 particles to dye-sensitized nanocrystalline photoelectrochemical cells was examined theoretically (60). Monte Carlo simulations reveal that the increase of absorption path length of photon in nanocrystalline films and optical confinement due to total reflections at solar cell surfaces improve light absorption in the sensitized films remarkably. Contribution of optical confinement to the improvement is much greater than that of the increase of absorption path length. Quantum efficiencies were calculated, considering the recombination of electrons in the nanocrystalline films. The application of light scattering improves the quantum efficiencies remarkably, especially in long wavelength lights. Distribution of light absorption in the scattering films were also studied, which represented as exponential expressions due to light reflection in vicinities of transparent conductive oxide (TCO) electrodes. Optical confinement decreases the light reflections and improves light absorption next to the (TCO) electrodes where generated electrons can diffuse without recombination.

A comprehensive analysis of the diffusion and migration process in the steady state operation of mesoporous photochemical solar cells has been studied (61). The porous nature of the semiconductor plays an important role in this process. Efficient design characteristics for such cells were obtained in order to minimize the concentration overpotentential, thus minimizing one of the sources of loss in such cells. The geometric and structural properties of the photoanode as well as the relative position of the counter-electrode with respect to the mesoporous film photoanode could be better exploited towards an efficient operation of the solar energy conversion device. The repercussions of the variation of solar cell design parameter were illustrated experimentally by the performance of practical application devices. These serve as an evidence towards the plausibility and the validity of a mass transfer model for the electrolyte function in nanocrystalline PECs.

The effects of a number of parameters on the magnitude of the dark current arises from the reduction of I_3^- at the dye-sensitized TiO_2 photoanode were studied by **Stanley** et. al. (62). Propylene carbonate, ethylene carbonate, acetonitrile and mixtures of these were all tested as solvents for the redox couple. With the expcetion of acetonitrile, which produce a slightly greater dark current, there was little variation in the dark current across the range of solvents tested. Propylene carbonate and ethylene carbonate produced significantly greater photocurrent than acetonitrile. Deoxgenation caused higher dark currents at potentials more reducing than – 0.7 V but had little effect on the photocurrent. Pretreatment of the electrodes with 4-tert-butylpyridine had little effect on the dark current.

Dye-sensitized colloidal TiO_2 film electrodes using a Ru(bpy)-complex were used as photoanodes in photoelectrochemical solar cells. The cells were prepared by **Hagfeldt** et. al.(5). An overall light-to-electric energy conversion efficiency of 7% in 1000 W/m^2 light from ELH lamp was obtained.

A new low cost solar cell used for power generation application was prepared **Knodelr** et. al.(63) using optimized electrodes made by screen-printing techniques, an efficiency of 9.4% was obtained for small electrodes

(0.5cm^2). Lifetime of more than 10 months without degradation was achieved at the EPE Lausanne using this type of cell.

Photovoltic cell created from low to medium-purity materials through low-coast process, which exhibits a commercially realistic energy-conversion efficiency was studied (64). The device is based on a 10-μm-thick, optically transparent film of TiO_2 particles a few nanometers in size, coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting. Because of the light surface area of the semiconductor film and the idea spectra characteristics of the dye, the device harvests a high proportion of the incident solar energy flux (46%) and showed exceptionally high efficiencies for the conversion of incident photons to electric current (more than 80%). The overall light to electric energy conversion yield 7.1-7.9% in simulated solar light and 12% in diffuse daylight. The large current densities (greater than 12 mA cm^{-2}) and exceptional stability (sustaining at least five million turnovers without decomposition), as well as the low cost, make particle applications feasible.

Resonance Raman and time-resolved Raman spectroscopies have been used to study the surface interactions of substituted bipyridyl complexes of ruthenium (II) as sensitizers with the colloidal semiconductor TiO_2 by **Umapathy** et. al.(65). It has been found that the adsorption of ruthenium (II) tris([2,2`-bipyridyl]-4,4`-dicarboxylate) (RB4H) into a colloidal TiO_2 surface was through the solvation layer, whereas cis-diaquaruthenium (II) bis ([2,2`-bipyridyl]-4,4`-dicarboxylate) (RBDA) adsorption was via the water ligands of the complex. The transient Raman spectrum of the metal-ligand charge-transfer triplet excited state of the ethyl ester of RB4H was reported. Analysis of the spectrum provided conclusive evidence for the excited electron being localized on one of the ligands and the photosensitization of

TiO_2 by RB4H and RBDA has been studied by using time-resolved resonance Raman spectroscopy.

Enea et. al.(66) discovered that the laser dye coumarin 343 sensitizes the visible light induced injection of electrons in the conduction band of TiO_2 films with a very high yield. The incident photon to current conversion efficiency (IPCE) exceeds 70% in the entire wavelength domain between 400 and 500 nm. It was as high as 83.5% around the absorption maximum of the dye, i.e. 440 nm. These unprecedentedly high current yields arise efficient light collection by the dye attached to the surface of the TiO_2 film and practically unit quantum yield for charge injection. Factors contribution to the unusually high visible light harvesting efficiency of the dye-coated TiO_2 films, which was related to their specific surface texture, were scrutinized.

The relation between the structure and photoelectrochemical properties of two dyes, cis-dithiocyanato-N,N`-bis(4,4`-dicarboxyl-2,2`-bipyridyl)Ru (II) and cis-dithiocyanato-N,N`-bis(4,4`-dicarboxyl-2,2`-bipyridyl)-(4,4`-di((N,N`-methylphenylamino)methylene)-2,2`- bipyridyl Ru(II) was examined and compared under the same conditions (67). Data showed that the photophysical properties (including molar extinction coefficients ε_m and excited-state lifetimes) and photoelectrochemical properties(including short-circuit photocurrent, open-circuit photovoltage, incident monochromatic photon to current conversion efficiency, overall energy conversion yield (η_y) and transient photocurrent) were changed greatly only due to an acceptor replaced by a donor in one of polypridyl of the Ru (II) complex, suggesting that the molecular design in energy conversion is very sensitive.

Dye-sensitized nanocrystalline TiO_2 solar cells (DSSCs) based on novel coumarin-dye photosensitizers was studied by **Hara** *et. al.* (68). It was found that the absorption spectra of these novel dyes are red-shifted remarkably in the visible region relative to the spectrum of C343, a conventional coumarin dye. Introduction of a methine unit (-CH=CH-) connecting the cyano (-CN) and carboxyl (-COOH) groups into the coumarin framework expand the π-conjugation in the dye and thus resulted in a wide absorption in the visible region. These novel dyes was performed as efficient photosensitizer for DSSCs. A DSSC based on 2-cyano-5-(1,1,6,6,-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo(de)anthracen-9-yl)-penta-2,4-dienoic acid (NKX-2311), produced a 6.0% solar energy-to-electricity conversion efficiency (η_y), the highest performance among DSSCs based on organic-dye photosensitizer, under AM 1.5 irradiation (100 mW/cm^2) with a short-circuit current density (J_{sc}) of 14.0 mA/cm^2, an open circuit voltage (V_{oc}) of 10.0 v and a fill factor of 0.71. It also suggested that the structure of NKX-2311 whose carboxyl group is directly connected to the -CH=CH- unite, is advantageous for effective electron injection from the dye into the conduction band of TiO_2. In addition, the cyano group, owing to its strong electron-withdrawing ability, might play an important role in electron injection in addition to a red shift in the absorption region.

Tesfamichael *et. al.*(69) characterized a dye-sensitized nanocrystalline titania film used in prototype photoelectrochemical solar cell production. It was found from transmission electron microscopy that the particles were seen as a mixture of tetrahedral and rhombohedral geometries with size distribution in the range between 10 and 25 nm. where, these particles were identified by X-ray diffraction as nanocrystals of anatase and brookite phases. The film was sensitized with a ruthenium (II) based chromophore for different times (between 0.5 and 24 hr.) and the penetration and coverage of the dye was studied using secondary ion mass spectroscopy. The dye was found to percolate through the whole of the titania film and was distributed uniformly. The film was determined and found to be 1 wt % Ru on maximum sensitization. The optical properties of the dye-sensitized films were also measured which resulted in an increase of absorbance and a decrease of transmittance for dyeing times up to 8 hr. Beyond this time the values remained unchanged and thus a semi-transparent film with luminous transmittance between 0.12 and 0.60 were obtained.

I-3. Aim of Work:

Due to that the mirrors or lenses require direct sunlight and direct tracking of the sun. And because, PMMA bears all properties required for good luminescence solar collectors (LSC) base material (e.g. highly transparent and high refractive index) and it is easy to prepare PMMA sheets of desired shape and size. So that the aim of this work is to evaluate the properties of LSC's prepared by casting method in which a thin film of PMMA doped with different organic dyes were used. The work include also studying the electrical and optical properties to give more information about the transition mechanism within the wide band gap of LSC materials to attain the best conditions under which these LSC's will have high thermal stability, photostability and enhance the solar cell conversion efficiency. The large scale use of photovoltaic devices for electricity generation is prohibitively expensive at present. So that this work is also concentrate in preparation of photoelectrochemical solar cell based on dye sensitization in nanocrystalline TiO_2 film. This film has attracted considerable interest as a potential high efficiency, long term stable and low cost alternative to conventional solid state solar cells. The effect of chemical structure of the dyes used on the properties investigated is one of our main target in this work.

Theoretical Review and Calculation Methods

Polymers are compounds whose molecules are sequences of a large number of recurring identical atomic grouping joined through chemical bonds (70). The recurring atomic grouping that make up a polymeric chain have come to be known as repeating or repeat units (monomeric units). It should be noted that very frequently the repeating unit differs substantially from the monomer, the polymerization of which leads to the formation of a polymer.

Polymer structure can be classified into three groups: liner polymer, branched polymer and cross-linked polymer. Three major structures are illustrated in Fig. (II-1). And according to the order in which the repeating units are arranged in chain, polymers are classified into regular and irregular (random) structures.

II-1. Conduction Mechanisms in Amorphous Solids

Organic compounds have conductivities eighteen orders of magnitude smaller than those of metals, and the polymeric subgroup falls at the low-conductivity end (3). Electrical conduction may occur through the movement of either electrons or ions. In each case, however, a suitable starting point for discussion of the conduction process is the basic equation:

$$\sigma = ne\mu \qquad (II.1)$$

where the conductivity σ is resolved into three factors: the charge e, concentration n and drift mobility μ of the carriers. The latter parameter characterises the ease with which charge species will move under the influence of the applied electric field and is usually expressed as a velocity per unit field ($m^2\ V^{-1}\ s^{-1}$). There may be contribution to the conductivity from several different types of carrier, notably electrons and holes

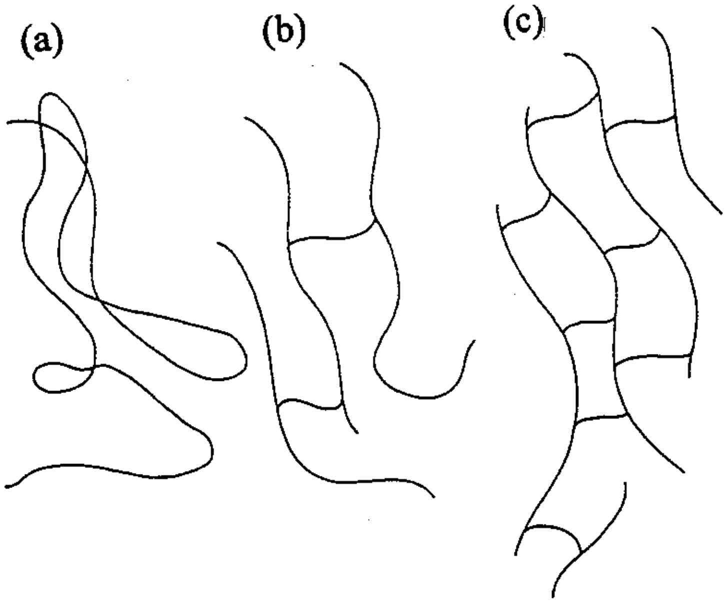

Fig. (II-1) Structural formulas of (a) linear polymer (b) branched polymer and (c) cross-linked polymer.

energies E_C and E_V the electron and hole mobility drop sharply from a low-mobility band transport with finite mobility at $T = 0$ to a thermally activated tunneling between localized gap states which disappears at $T = 0$. The mobility edges define a mobility gap ($E_C - E_V$) which contains only localized states. The other principle feature of this model was the existence of "mobility edges" at energies in the band tails. These defined as the critical energies separating localized states from extended state. The difference between the energies of the mobility edges in the valence and conduction bands is called the "mobility gap". Mott and Davis (74) believed that an ideal amorphous solid in which all bonds are saturated and which there are no long-rang fluctuations should have a density of states as in Fig. (II-2-b) with a true gap. Deep tails should arise only from cross density or bond-angle fluctuations.

II-1-a-ii. Davis and Mott model (75)

Alternative suggestion to the CFO model for states in the gap are shown in Fig. (II-2-c,d). In Fig. (II-2-c) a strong distinction is made between localized states, which originate from lack of long-range order and others which are due to defects in the structure. The first kind of localized states extended only to E_A and E_B in the mobility gap. The defect states from longer tails but of insufficient density to pin the Fermi level (E_F).

II-1-a-iii. Marshall and Owen Model (76)

In this model, shown in Fig. (II-2-d), the position of the Fermi level is determined by bands of donors (E_Y) and acceptors (E_X) in the upper and lower levels of the mobility gap, respectively. The concentrations of donors and acceptors adjust themselves by self-compensation to be nearly equal so that Fermi level remains near the gap. Single and double occupancy conditions lead to two bands separated by appropriate correlation energy of hubbard U (77).

II-1-b. Hopping Conduction

For a random distribution of atoms the density of electronic energy state tails, into what is normally the forbidden zone, and the electrons in these tails are localized. There is then not so much an energy gap as a mobility gap. In other words there is an intermediate range of electronic energy states in which mobilities are very low. Only when electrons are excited to higher energy states, in which mobilities are higher, can appreciable conduction occur. Conduction, via localized electrons implies discrete jumps across an energy barrier from one site to the next Fig. (II-3). An electron may either hop over, or tunnel through the top of the barrier, the relative importance of these two mechanisms depending on the shape of the barrier and the availability of thermal energy. This thermally activated type of mobility will increase with temperature (3).

It is assumed that the density of states near the bottom of the conduction band, as shown in Fig. (II-4-a), has the form (3):

$$N(E) = C(E - E_A)^n \qquad \text{(II.2)}$$

At E_C the decay length of the localized states (γ^{-1}) goes to infinity, i.e. $\gamma^{-1} \rightarrow \infty$ and the states become extended; below and close to E_C, it falls as $(E_C-E)^{2/3}$. Deeper in the tail, γ^{-1} is assumed to be constant. Fig. (II-4-b) shows the variation of the decay length (γ^{-1}) with the energy. The conductivity associated with band tail hopping can be expresses as (78,79):

$$\sigma = ne\mu_{hop} \qquad \text{(II.3)}$$

where n is the number of electrons in the tail and is given by:

$$n = \int_{E_A}^{\infty} eN(E)\exp[-(E - E_F)/K_BT)]dE \qquad \text{(II.4)}$$