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In past, organic semiconducting molecules have been studied extensively in solution. Where ease of isolation of molecule in dilute form and aggregation of molecule in concentrated solution have exhibited interesting optical properties particularly fluorescence. Attempts have also been made to put the dyes in solid matrices since they have many advantages in solid state electronic devices from both technical and cost point of views. Silica is specially one of the possible candidate as the solid matrix since it provides high photostability. However, poor solubility of organic materials in silica causes a major problem with optical quality. The polymer is the best alternative for silica and also serves as solvent where organic molecules could be dispersed to prepare homogeneous polymer films of organic fluorescent materials. In the present studies polynuclear aromatic hydrocarbon (PAH) solutes were used as dopant in polymer thin films prepared by spin coating technique. The structural and optical properties have been studied by X-ray diffraction, absorption and fluorescence spectroscopy.

The pyrene is the Model PAHs used in the studies. The monomer and excimer emission was observed from the polystyrene films, when doped by varying wt % of pyrene. Both emissions are similar with those reported for pyrene in dilute and concentrated solution respectively, as well as with LB film studies. It is interesting to note that both monomer and excimer emission is observed from the same film and the critical wt % of pyrene giving transition from monomer to excimer was determined. The dependence of emission intensiy on weight percent of pyrene in film was established both at monomer and excimer emission wavelength. It is also observed that the emission properties also depend upon thickness of the film unlike the solutions. Absorption studies of the pyrene doped polystyrene films indicated absence of aggregation in ground state even at high wt % and from the spectrum energy band gap of pyrene molecule has been calculated.

The photoluminescence from doped matrices is generally complicated due to rigidity of matrix and due to strong interactions between active guest species. With a view to understand the effect of interaction between the components of mixture in polymer matrix, the fluorescent poly aromatic hydrocarbons (PAHs) known to undergo energetic interaction and or association with pyrene were chosen as second solute in polymer matrix. The fluorescence behaviour of second solute material in polystyrene were studied first without pyrene and then with pyrene. The fluorescent PAHs selected as second solute are perylene, naphthalene, biphenyl, 9-anthracene carboxylic acid.

Fluorescence spectrum of perylene doped polystyrene is structured and similar with those reported for its solution in inert solvent and for thin micro crystals. The spectrum has been modified when its wt % in polystyrene was increased. The band at 450 and 480 nm are quenched with perylene concentration and the spectrum becomes featureless with maximum emission at 510 nm. This band has been assigned to an excited dimer because the absorption studies of perylene doped films have shown modification in the absorption spectra. The well known Y excimer emission of perylene expected to occur at 560 nm is not observed in the spectrum of perylene even at highest possible concentration in the polystyrene film.

Fluorescence spectra of pyrene and perylene doped polystyrene films were monitored at excitation wavelength 340 nm which corresponds to pyrene excitation energy. The wt % of pyrene in the film was kept constant to a value 0.17275 and in absence of perylene such film exhibited monomer emission. The presence of perylene quenched the pyrene monomer fluorescence and in addition to that a weak tail is appeared towards red. Increase in wt % of perylene in the film has increased the intensity and tail modified into an intense broad band having maximum emission at 520 nm. The quenching of monomer emission is explained on the basis of excitation energy transfer between pyrene and perylene while broad band at 520 nm is attributed to exciplex formation between excited perylene and ground state pyrene and subsequent exciplex emission.

Naphthalene and pyrene doped polystyrene films :

Naphthalene in polystyrene matrix fluoresce in UV and violet region with maximum emission at 314 nm. The absorption and excitation spectroscopy of naphthalene polymer films indicated that the molecule exists in isolated form and possibility of formation of aggregates even at higher concentration with itself is negligible. The fluorescence spectrum of naphthalene even at higher wt % remained unmodified. But the naphthalene in presence of pyrene has given very interesting results. The excitation energy of naphthalene is trapped by pyrene in matrix and excited pyrene molecule is formed. The excited pyrene associate with ground state naphthalene and undergo excitation energy relaxation to form an excited bimolecular species. This exciplex deactivates to give emission at 480 nm.

The intensity of broad exciplex emission band found increased with increase in concentration of naphthalene in the film. This observation led to believe that pyrene associates with naphthalene to form an exciplex.

Biphenyl in polystyrene film :

Biphen~~d~~yl absorption spectrum is exceptional as it is a broad band indicating association in the ground state. However, biphenyl exists an isolated molecule in ground state because absorption spectrum of biphenyl film, biphenyl dilute solution and excitation spectrum are identical. The broad band is due to random orientation of phenyl rings not being in the same plane. However, the fluorescence spectrum of the film containing lower wt-percent is a broad band and as wt % in the film increases the spectra becomes structured. The structured nature is due to the fact that the phenyl rings become more coplanar.

Exciplex emission from biphenyl-pyrene in polystyrene matrix :

The fluorescence studies of polystyrene films containing pyrene 0.1728 wt % corresponds to its monomer emission and varying amounts of biphenyl, indicated the quenching of pyrene emission and exciplex formation as a broad structureless band appeared towards red peaking at 458 nm. In the excited state at higher wt % of biphenyl its molecule may become more co-planer and undergo association with pyrene to form an exciplex. The association with pyrene to form an exciplex. The association between these molecules is probable because both molecules favour strong lateral π-orbital overlapping. In addition at higher concentration of biphenyl the molecules of biphenyl and pyrene are brought close together in rigid polymer matrix.

Fluorescence Studies of 9-ACA in Polymer Film :

The fluorescence properties of 9ACA are interesting to the substituent –COOH and vary in solutions in aprotic and protic solvents. Attempts to obtain these properties in polymer films prepared from different solutions were successful. The polystyrene films prepared from benzene solution containing 9ACA have shown its week emission at 412 nm at lower wt % in film. While the polystyrene films containing higher wt % of 9ACA have shown intense broad, structureless band peaking at 468 nm. Films prepared from polyvinyl alcohol in ethyl alcohol have shown single sharp band peaking at wavelength 412 nm. The increase in concentration of solute quenches the intensity of this band and at higher wt % a broad band peaking at 490 nm appears. In alcohol, the 9-ACA dissociates and undissociate form undergo association to form dimeric species exhibiting broad band emission at different wavelength. The films prepared from alcohol-water solution of 9ACA and polyvinyl alcohol (PVA), shows structured sharp band peaking at 412 nm in the spectra, when 9ACA wt % is lower in the film. However, the films containing higher wt % of 9ACA shows structured anthracene like emission exactly similar with anthracene solution. The broad bands corresponding to excimer or hydrogen bonded dimer are not seen in the spectra. It seems that water-alcohol prevents the aggregation of molecules. The mechanism suggested for emission is confirmed by absorption and excitation spectroscopy. The dual luminescence exhibited by 9ACA molecules dispersed in different polymers is interesting. The colour and intensity of polymer doped by 9ACA could be monitored by selecting properly polymers and solvents to prepare solutions for film coating.

9Anthracene carboxylic acid and pyrene interactions in polystyrene solutes. ? The monomer fluorescence of pyrene has been quenched by 9ACA in polystyrene film prepared from benzene solution. As wt % of 9ACA in film increases, the extent of quenching increases and simultaneously a broad band peaking at 468 nm appears. The intensity of broad band increases with wt % of 9 ACA. The observed quenching of pyrene monomer fluorescence suggests EET from pyrene to 9ACA. The 9ACA excited molecules thus formed become more coplanar and undergo twisting so as to form a conformer responsible to a broad band appeared at 468 nm.