CHAPTER 7

SUMMARY OF THE PRESENT WORK AND SUGGESTIONS FOR FUTURE WORK

7.1 SUMMARry OF THE PRESENT WORK

The spectral characteristics of these dyes belonging to triarylmethane family, azine family, acridine family, quinolone family and azo family in monomer compositions in nBA and in PMMA modified with nBA are studied and the results of dyes in PMMA modified with nBA are compared with dyes in monomer compositions and in nBA. These dye doped polymer rods in the form of rectangular shape with 0.05 mM dye concentration are synthesized. The steady state absorption and fluorescence spectra of these dyes in liquid and in solid environment are recorded. From the absorption and fluorescence spectra the spectral parameters such as absorption peak wavelength, absorption spectral bandwidth, oscillator strength, fluorescence peak wave length, fluorescence spectral bandwidth and Stoke’s shift are calculated and these results are intercompared.

The absorption and fluorescence spectral profiles of triarylmethane dye in liquid and solid environment are identical. This indicates that at low concentrations, these dyes exists only in their monomeric form and the dye within the polymeric matrix distribute themselves in a similar way to that of the dye molecules in dilute solution. The absorption spectra of triarylmethane dyes in solid matrix showed a blue shift when compared to that in a mixture
of MMA and nBA. This may be due to the increase in the rigidity of the polymeric matrix.

The fluorescence spectra of triarylmethane dyes showed a blue shift compared to that in a mixture of MMA and nBA. This may be due to decrease in dielectric constant of the solid matrix. The dielectric constant of the liquid medium is higher than that of the solid medium. The absorption spectral profiles of all triarylmethane dyes except victoria blue in solid matrix and fluorescence spectral profiles of all triarylmethane showed broad bandwidth compared to that in a mixture of MMA and nBA. This may be due to the inhomogenous distribution of the dye molecule in the polymer matrix. This inhomogenous broadening is due to the distribution of the dye molecules surrounded by host media having different dielectric character. It is known that complicated organic molecules in solid environment may be considered as an ensemble of centers differing in resonance frequencies of fundamental transitions, which cause inhomogenous broadening.

The fluorescence bandwidth of acridine orange in solid matrix is narrower than those in liquid media. This may be due to the restricted mobility of the dye molecule in the solid matrix.

The Stoke’s shift of triarylmethane dyes except crystal violet and malachite green in solid matrix is less than that in a mixture of MMA and nBA. This may be due to, as the Stoke’s shift depends on the size, polarity and relocation time of the additive molecule.

The fluorescence quantum yield of triarylmethane dyes except crystal violet in solid matrix is higher than that of the dyes in a mixture of MMA and nBA. This may be due to the molecule rigidity of the dye molecule in the solid matrix, which appears to reduce the non-radiative relaxation processes that can compete with fluorescence. Due to high mobility of the
amino group in these dyes, there is a considerable increase in the rate of internal conversion. For these dyes, the mobility of the chromophore is restricted and the fluorescence efficiencies is increased considerably. The increment of the rigidity of the matrix prevents the internal rotation of the excited dye, so that non-fluorescent deactivation of the excitation energy via rapid internal rotation or conformation changes are avoided. The added molecular rigidity of the dye in PMMA appears to reduce the non-radiative relaxation processes competing with fluorescence.

The fluorescence quantum yield of cresyl violet, crystal violetm, acridine orange, LD 473methyl orange in solid matrix is less than that in liquid medium. This may be due to re-absorption process, because the overlapping of the absorption and fluorescence spectra of these dyes in solid matrix is higher compared to that in the liquid media.

Azine dyes showed a blue shift in the peak wavelength of absorption and fluorescence in solid matrix when compared to the liquid media. The molar extinction of cresyl violet and methylene blue in solid matrix is less compared to that in a mixture of MMA and nBA and distilled water respectively. This may be due to the polymerization process, which affect the dye concentration in the polymerization tube and the dye may get bleached during the polymerization process.

The fluorescence bandwidth of cresyl violet and methylene blue in solid matrix is broader than that in the liquid medium. The fluorescence quantum yield of methylene blue in solid matrix is higher compared to that in distilled water. The absorption spectral bandwidth of methyl orange, LD 473 in solid matrix is broader than that in a mixture of MMA and nBA. The absorption bandwidth of acridine orange and congo red is narrower than those in a mature of MMA and nBA. This may be due to the restricted mobility of the dye molecules and the decrease in dielectric constant of the material.
The bi-exponential decay of crystal violet, malachite green, methyl orange, acridine orange, night blue and congo red in a mixture of MMA and nBA and methylene blue in PMMA modified with distilled water may be due to the presence of bleached and unbleached dye molecules in the excited state. This is also due to the formation of complex between the dye and the solvent mixture and the presence of two emitting species in the excited state.

The nonlinear properties of these dyes in liquid and solid medium are studied under He-Ne laser excitation, using Z-scan technique. The dyes acridine orange, cresyl violet, crystal violet, malachite green, night blue, methylene blue and congo red showed a negative nonlinearity, which is observed from the Z-scan trace itself. The trace shows a pre-focal transmittance maximum (peak) followed by a post-focal transmittance maximum (valley), indicating the dyes are of negative nonlinearity.

The Z-scan trace of the dyes methyl orange, victoria blue and LD 473 shows a pre-focal transmittance minimum (valley) followed by a post-focal transmittance maximum (peak). This clearly indicates clearly that the dyes are of positive nonlinear sign of nonlinearity.

In all the dyes there is a hike in the value of the $\Delta T_{pv}$ for the dye doped polymer film when compared to the dyes in nBA. This hike may be due to the heat dissipation in liquid is fast when compared to the polymer film. And it is this heat inducing a hike in $\Delta T_{pv}$ value in polymer film.

The optical nonlinearity of the dye may be due to laser heating induced nonlinear effect. A laser beam, while passing through an absorbing media, induces temperature and density gradients that change the refractive index profile. This intensity –induced localized change in the refractive index results in a lensing effect on the optical beam.