

# Photoinduced Electron Transfer Processes in Polymeric Nanoparticles

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The study of fast reactions involving radical pairs of low molecular weight (neutral or ionic) in polymer matrices is of great importance in understanding the mechanisms of the mechanical, thermal or photoinduced degradation of synthetic polymers. Likewise, understanding the phenomenon of charge transport through in solid matrices has been of large importance in the development of photoconductive polymers and in the design of optoelectronic devices.

We present here preliminary studies on photoinduced electron transfer processes occurring in nanoparticulate polymeric matrices. Two different types of nanoparticles were synthesized copolymerizing: methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), (1) and (2); the last monomer especially synthesized for this study.



Syntheses were carried-out *via* the microemulsion polymerization technique (SDS micelles) and using the following monomer (molar) concentration ratios of (1) / (2) / MMA / EGDMA; nanoparticles type *a*: 1: 30: 80: 60 and type *b*: 1:0:110:60. This is, nanoparticles type *b* do not contain the electron donor monomer (2). The nanobeads were purified and characterized by light scattering and SEM microscopy. The estimated particles diameters are  $(10\pm 6)$  nm. The particles are readily dispersible in organic solvents (acetonitrile, dichloromethane, etc.). The average number of fluorophores (1) in the particles is around 1.4. The fact that (1) is covalently linked to the polymers was verified by (excitation) fluorescence anisotropy experiments.

The fluorescence spectra (exciting the anthracenyl group at 350 nm) of both types of particles are identical. However, the fluorescence quantum yield of particles *b* is  $\sim 8$  times larger than that observed for nanoparticles *a*. The decay time profiles measured ( $\lambda_{\text{exc}} = 350$  nm) show for both types of particles a complex behavior. However, they are very similar and from their analysis it is concluded that there are two populations of fluorophores (1) in the polymeric matrices, one characterized by a  $\tau \sim 5$  ns and the second by a  $\tau \sim 17$  ns. The fluorescence spectrum obtained for particles *a* exciting at 310 nm (aromatic amine chromophore) shows the emission of the amine but also that of the anthracene. The results above suggest that the decreased fluorescence quantum yield observed for type *a* particles is due to a fast electron transfer reaction between the anthracene singlet excited state and amino groups in close contact. The fluorescence quenching of particles *b* by *N,N*-dimethylaniline in acetonitrile solutions was also studied. The Stern-Volmer plots obtained using stationary and dynamic (TCSPC) techniques do not agree. The analysis of the quenching data was carried out using a (modified) model proposed by J. N. Demas et. al. It is concluded that the short lifetime (1) population is quenched at rates similar to the observed in fluid media, while the long time living excited states are quenched  $\sim 100$  times slower. The electron transfer nature of the quenching process was confirmed by ( $\mu\text{sec}$ ) laser flash photolysis experiments. In the short time scale the transient spectra show absorptions that correspond to the anthracene anion and DMA cation radical.