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Irradiation of MEH-PPV with gamma rays in alkyl halide

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Abstract – In this Work, the effect of gamma radiation on the optical properties of poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylenevinylene] (MEH-PPV) solutions is studied. The samples were irradiated at room temperature using a ^{60}Co gamma ray source. The irradiation of (MEH-PPV) solutions of alkyl halide solvents with gamma rays causes blue-shifts of their UV-VIS absorption spectra main peak and different effects can be observed. The results show that the effects depend on the nature of the solvent and the polymer concentration. The photochemical reaction was characterized by ^{1}H NMR spectroscopy and was pointed as halide addition in the polymer chain.

The optical properties of conjugated polymers have been subject to extensive studies since the advent of its use in photonic applications. When poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylenevinylene] (MEH-PPV) solutions in halogen containing solvents are irradiated with ^{60}Co gamma rays with doses up to 50 Gy, blueshifts of its UV-VIS absorption spectra main peak can be observed. We compared the gamma irradiation effects in the UV-VIS spectra of different MEH-PPV solutions; in dichloromethane, chloroform, dibromomethane, bromoform and toluene. Shifts in the absorption peak of up 360 nm were observed depending on solvent and MEH-PPV concentration.[1] The changes in UV-Vis absorption spectra were compared and the effects were evaluated.

The results show that the effects of gamma irradiation on MEH-PPV solutions in alkyl-halide solvents are greater than those in toluene irradiated with the same dose. The spectra changes observed were greater for solutions in solvents with bromine (CH_2Br_2 and $CHBr_3$) atoms than those in solvents with chlorine atoms (CH_2Cl_2 and $CHCl_3$) and concentration influences can be observed. ^{1}H NMR spectroscopy of MEH-PPV solutions in deuterated chloroform ($CDCl_3$) and in $CHBr_3$, before and after irradiation with gamma rays, was performed to identify the chemical reaction involving the polymer and the halogen atoms of the solvents. NMR spectra analysis of MEH-PPV in CHX_3 where X is Cl or Br indicated that the reaction is a addition of halogen atoms in the polymer chain, CH_2X_2 and halogenated MEH-PPV. The GPC was realized and clearly shows that the average molecular weight of MEH-PPV decreases after gamma irradiation, in this case, from Mn = 61000 to Mn = 43000 g/mol.

The reaction identified by NMR spectroscopy points that the effective conjugation reduction responsible to the shifts in the UV-VIS spectra observed for all but toluene solutions showed above is due to changes in the interaction of the polymer with the solvents. The analysis of ^{1}H NMR and GPC confirm the reaction between solvent and polymer as well as polymer chain scission, after irradiation. The solvent in such cases must be treated as the main reagent in the system, and its concentration is crucial to the efficiency of the photoreaction.

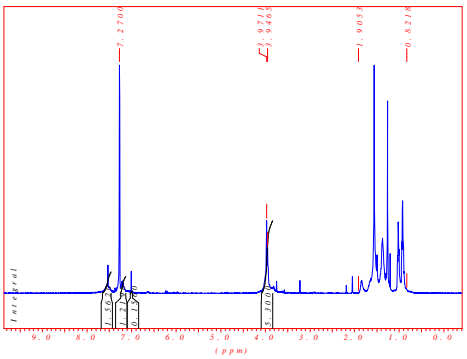

Figure 1: 400 MHz ^{1}H NMR spectra of a MEH-PPV solution in $CDCl_3$ before irradiation.

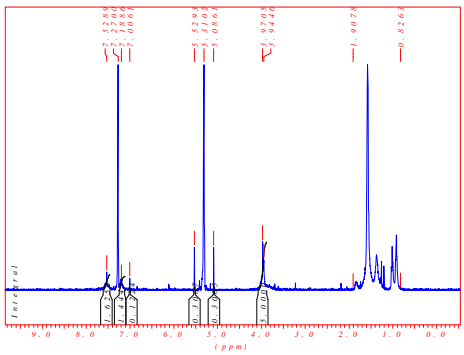

Figure 2: 400 MHz ^{1}H NMR spectra of a MEH-PPV solution in $CDCl_3$ after 50 Gy gamma rays irradiation.

[1] E.A.B. Silva; J.F. Borin; P. Nicolucci; C.F.O. Graeff; T. Ghilardi Netto; R.F. Bianchi; App. Phys. Lett. 86 (2005) 131902-1
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