

Control of the composition of the grafted organic layer by diverting the reactivity of aryl radicals

Fetah Podvorica^{1,2,4}

Avni Berisha^{1,4}

Dardan Hetemi^{3,4}

¹Chemistry Department of Natural Sciences and Mathematics Faculty, University of Prishtina, rr. "Nëna Tereze" nr. 5, 10000 Prishtina, Republic of Kosovo

²Academy of Sciences and Arts of Kosova, Rr. "Agim Ramadani" nr 305, 10000 Prishtina, Republic of Kosovo

³Pharmacy Department of Medical Faculty, University of Prishtina, rr. "Nëna Tereze" nr. 5, 10000 Prishtina, Republic of Kosovo

⁴NanoAlb-Unit of Albanian Nanoscience and Nanotechnology, 1000 Tirana, Albania

fetah.podvorica@uni-pr.edu

Aryl radicals derived from aryl diazoniums during their electrochemical or spontaneous reduction on the electrode surface at the electrode potential about 0 V/SCE in aprotic or aqueous solution, in general, are able to attack the material surface and create a polyphenylene layer. [1] However aryl diazonium salts that contain two methyl substituents in the ortho position to the diazonium group, 2,6-dimethylbenzodiazonium salt, generate 2,6-dimethylphenyl (2,6-DMP) radicals that are unable to react with electrode surface due to their steric hindrance. These highly reactive radicals are prone to abstract hydrogen atom from the solvent, acetonitrile or methyl amine that enabled the generation of cyanomethyl or aminomethyl radicals that are attached on the electrode surface, see figure 1. [2] Therefore, by diverting the reactivity of aryl radical one can change the composition of the grafted layer. 2,6-DMP radicals are also able to remove halogen atoms from alkyl iodides and bromides solutions in acetonitrile and form highly reactive alkyl radicals that tether electrode surface with alkyl moieties. [2,3]

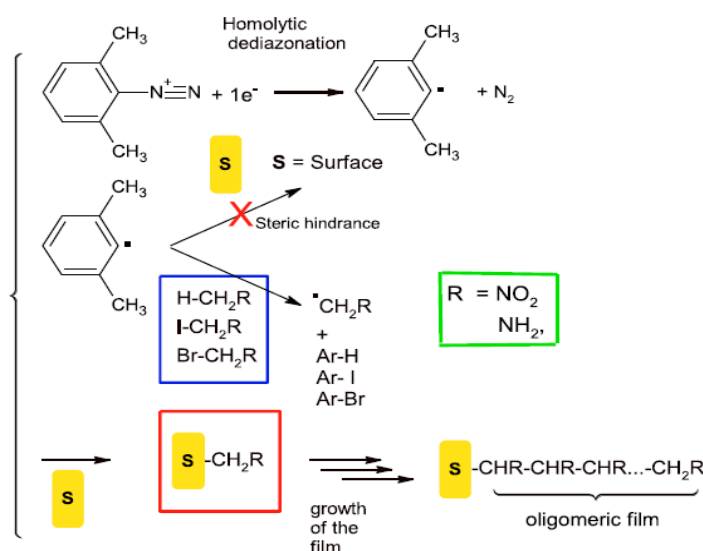


Figure 1: Grafting through C-H, C-I, C-Br activation with a sterically hindered aryl radical obtained by reduction of the 2,6-dimethylbenzen diazonium salt.

References

[1] Berisha A., Chehimi M., Pinson J. and Podvorica F. Book Chapter Bard AJ, Zoski CG. Eds., Electroanalytical Chemistry; 26 CRC Press: Boca Raton, FL, 2016.

[2] Electrografting of methylamine through C-H activation and oxidation to give highly aminated surfaces, J. Médard, A. Berisha, P. Decorse, F. Kanoufi, C. Combellas, J. Pinson, F. I. Podvorica, Electrochim. Acta 2020, 345, 136170-136180.

[3] Direct vs indirect grafting of alkyl and aryl halides, D. Hetemi, C. Combellas, F. Kanoufi, F. I. Podvorica, ChemPhysChem 2021, 22, 1844-1849.