

Indirect electrochemical grafting of organic molecules

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Aryl diazonium salts are considered as excellent reagents for surface modification due to their ability, once electrochemically or chemically reduced, to create aryl radicals that strongly attach to a variety of material surfaces (ranging from all types of carbon, metals and metal oxides, semiconductors and polymers). [1] As very reactive species, aryl radicals are prone to tether the substrate surface or to attach to already grafted aryl moieties and form a multi-layer. A part of aryl radicals generated near the electrode surface, may undergo other reactions in the solution such abstraction of the hydrogen atom from the solvent, acetonitrile or methyl amine [2,3] a vinylic monomer or an alkyl or aryl halide RX, or RX. These H or X atom abstractions enable the formation of alkyl radicals that react immediately with material surface. Last reactions are particularly advantaged when aryl radicals are prevented to react with substrate surface due to the steric hindrance, as is the case with 2,6-dimethylphenyl radicals issued from 2,6-dimethylbenzen diazonium salt (2,6-DMBD), figure 1. [4,5] This approach is important as it permits the indirect electrochemical grafting of alkyl and aryl groups at mild conditions via a radical crossover reaction and there is a high positive potential shift, > 1.7 V compared with direct electrochemical reduction of RX or ArX. [6] Recently we have been able to graft acrylate monomers or vinyl ferrocene onto gold, iron, copper and different carbon types by abstracting a H atom from acrylate or vinyl monomer. [7]

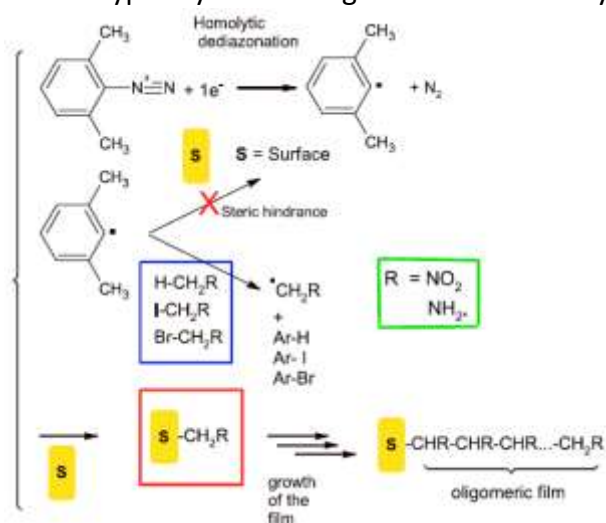


Fig. 1. Indirect grafting of solvent, alkyl or aryl halides through C-H, C-I, C-Br activation with 2,6-dimethylaryl radical obtained by electrochemical reduction of the corresponding diazonium salt. [5]

References

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