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GRAFTING OF VINYL MONOMERS ON PVC AND PVDF BY ATRP

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ATRP (atom transfer radical polymerization) has been recently used to prepare graft copolymers with regularly-spaced polymer chains from polymeric macroinitiators that have pendant chemical groups containing radically transferable halogen atoms [1]. The halogen atom serves as initiation site for the polymerization of side chains. ATRP employs the equilibrium between dormant alkyl halides and active propagating radicals to maintain a low concentration of active species. The activated radical species can either propagate or be deactivated to reform the dormant species. This process is catalyzed by a transition metal compound such as Cu-based species. The continuous development of more active and stable catalysts in ATRP has increasingly required a thorough knowledge of concurrent electron transfer reactions that can affect the catalyst performance. Special attention is paid to various phenomena including: (i) disproportionation, which is most pronounced in Cu-mediated ATRP, (ii) reduction of radicals to carboanions or carbocations, and (iii) radical coordination to the metal catalyst resulting in the interplay of a controlled radical polymerization mechanism [2,3]. It has been recently shown that an externally applied electrochemical potential can reversibly activate the copper catalyst for this process by a one-electron reduction of an initially added air-stable cupric species (Cu(II)/Ligand). In particular Gennaro and co-authors have shown that the polymerization kinetic can be changed modulating the external potential [4].
Our group has recently studied the stability of a Cu-based ATRP catalytic complex in two different solvents, namely NMP and MeCN. According to literature, these solvents behave differently regarding side reactions, such as disproportionation and comproportionation. The possible utilization of poly(vinylidenefluoride) (PVDF) and poly(vinylchloride) (PVC) as initiators was studied under different operative conditions in order to develop an electrochemically assisted atom transfer radical graft copolymerization (e-ATRP).

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