

Electroinitiated Polymerization of Vinyl Monomers
for the Preparation of Crosslinked Polymer Film Electrodes

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Electrochemical devices are used for solar cells, fuel cells, batteries, electrolytic cells and electronic display devices. In all of these devices the electrode reaction depends strongly on the nature of the electrode surface. Modification of electrodes allows increased control over electrochemical processes. Two recent reviews summarize work in the chemical modification of electrodes [1,2].

In 1978, Van De Mark and Miller reported the use of an adsorbed polymer as an electrode modification layer [3]. Since that first report, numerous electrochemists have prepared and studied electrodes coated with electroactive polymers [4,5,6,7].

One of the major reasons for interest in polymer-modified electrodes is the prospect for their use in surface electrocatalysis [8]. Criteria for useful catalyst supports in heterogeneous electrocatalysis are similar to criteria for heterogeneous thermal catalysis on polymer resin supports [9]. An ideal electrocatalytic system for use in synthesis would contain a thick, porous film of catalyst-containing material attached to an electrode surface. The catalyst throughout the film should be easily accessible to substrate species. In addition, charge transport and ion mobility within the film should be facile. One system which has promise in meeting these criteria is an electroactive, crosslinked polymer film adsorbed to an electrode in a swelling solvent.

There have been several reports of methods for obtaining crosslinked polymer films on electrodes. These include radiofrequency plasma polymerization [10], ultraviolet [11] and gamma [12] irradiation of polymer films, electrochemically induced dimer formation between polymer pendant groups [13], and electroinitiated polymerization of multifunctional electroactive monomers [14]. These methods produce useful films but are dependent upon the specific properties of the crosslinking agent used, or yield films of unknown structure.

The goal of the work reported in this seminar was to develop an electrochemical method that would be general for preparing polymer films and that would give films of known structure. Polyvinylbenzophenone has been used as an initiator precursor for bulk graft copolymerization. The poly-anion radical initiator was generated electrochemically for the polymerization of methylmethacrylate [15], and the polydianion initiator was generated by chemical reduction for the polymerization of styrene [16].

Based on the success with polyvinylbenzophenone in bulk anion polymerization, benzophenone was selected for use in the present study. Polydivinylbenzene-coated platinum electrodes were prepared from divinylbenzene by generating the benzophenone dianion electrochemically in N,N-dimethylformamide with tetrabutylammonium perchlorate

as electrolyte. The polymer was sulfonated by exposing it to a solution of chlorosulfonic acid in dichloromethane, then to a solution of water in acetonitrile [17]. The resulting crosslinked polystyrene-sulfonate film was studied by carrying out cyclic voltammetry in a solution of $\text{Ru}(\text{NH}_3)_6^{2+}$. The ruthenium complex was ion-exchanged into the film as shown by reversible one-electron oxidation for the ruthenium complex in the film. This wave remained when the electrode was placed in supporting electrolyte solution in the absence of dissolved $\text{Ru}(\text{NH}_3)_6^{2+}$.

Polyvinylferrocene was produced from vinylferrocene on pyrolytic graphite in the same way in acetonitrile. In the case of vinylferrocene, however, polymerization occurred to some extent even in the absence of benzophenone.

Many metal-phosphine complexes are known to be good catalysts for reactions that may be considered formally as oxidation-reduction reactions, such as the hydrogenation of olefins [18]. Possible electrocatalytic behavior of such complexes may be investigated by attaching them to a phosphine-containing polymer on an electrode surface. With this in mind, the monomer *p*-styryldiphenyl phosphine was synthesized [19] and polymerized [20] by a radical mechanism. Metal complexes of this polymer were prepared but electrochemical studies were thwarted by irreversible electron transfer and instability of the non-crosslinking films in swelling solvents. Work is continuing on these systems.

A possible general method has been developed for the preparation of crosslinked, polymer film electrodes. Sulfonated polydivinylbenzene was prepared as an ion-exchange resin film and is stable even in water, a swelling solvent for this polymer. Application of this method to the preparation of supports containing known electrocatalysts, such as polyvinylferrocene [10], and potential electrocatalysts such as metal-phosphine complexes holds promise for future work.

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