

## Induced Chemical–Electrochemical Process for the Formation of Electrically Conducting Ionomers

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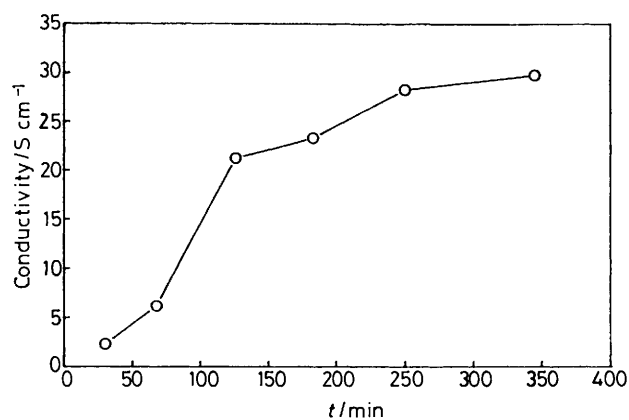
Electrically conducting ionomers, with conductivity higher than  $30 \text{ S cm}^{-1}$ , were prepared in aqueous solutions by a two-step chemical–electrochemical process; polypyrrole was implanted chemically in home-made ionomers in an oxidative polymerization stage, while the reduced polymerization reagent was re-oxidized anodically to close a catalytic cycle.

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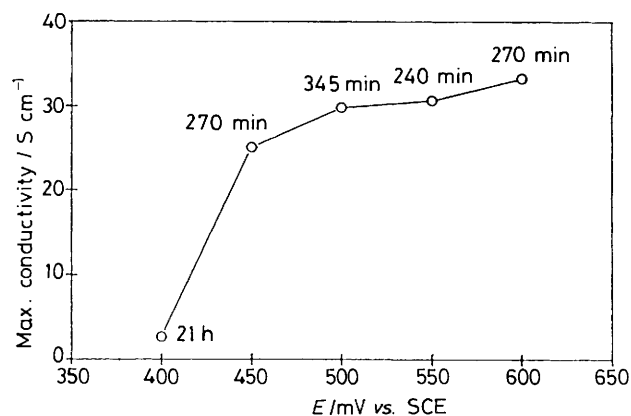
Inherently Conducting Polymers are currently being investigated world-wide owing to their practical and theoretical significance.<sup>1</sup> Good mechanical properties and stability as well as processibility are essential for practical purposes. The utilization of such polymers is currently limited by their poor mechanical properties and lack of processibility.

In order to improve their mechanical properties, inherently conducting polymers have recently been reinforced by implanting a conducting polymer in an insulating host

matrix.<sup>2,3</sup> This method is, however, limited by the requirement that charged dopant, neutral monomer, and sometimes an oxidation agent, which have significantly different hydrophilicity, should diffuse into the insulating film.<sup>4</sup> This obstacle can be partly avoided by the use of an insulating film to which the dopant is already bound to the polymer backbone, *viz.* ionomers. The predicted advantages for the ionomer/conducting polymer composite are that the preparation of the composite is no longer dependent on the diffusion



**Figure 1.** Variation of the film conductivity during the reaction. Solution composition: 10 mM FeCl<sub>3</sub> and 80 mM pyrrole; film composition: PE film grafting 165%, sulphonation 117%, loading 4.65 mequiv./g; applied potential 500 mV vs. SCE.



**Figure 2.** Variation of the ionomer maximum conductivity with the potential applied during the polymerization. Solution and film compositions as in Figure 1.

rate of the dopant in the film, and that the doping-undoping kinetics are enhanced because the counter-ions which move during this process are small.

Chemical methods for oxidative polymerization of pyrrole have been known for many years.<sup>5</sup> Various oxidizing agents have been used to produce 'pyrrole black,' including iron(III) chloride, which has been used extensively recently to prepare polypyrrole (PPy).<sup>6,7</sup> In all the reported data the ratio of iron(III) to pyrrole exceeded 2.25, a value which is derived from the stoichiometry of the reaction. Although a part of the iron species might be incorporated as a dopant in the polymer (e.g., [FeCl<sub>4</sub>]<sup>2-</sup>), most of the iron(III) is reduced to iron(II) in the solution and thus can be recycled electrochemically. The overall process, therefore, can be envisaged as being composed of two steps: a chemical step, in which the polymerization of pyrrole by iron(III) is carried out, and an electrochemical step which maintains a constant concentration of this oxidizing agent. This, so-called induced chemical-electrochemical process is especially suitable for the preparation of conducting ionomers.

Home-made ionomers were prepared in a two-step process. (i) Various commercial polyethylene (PE) films were grafted with polystyrene (PS) using a pre-radiation technique. The degree of grafting in the PE/PS films was controlled by the radiation dose, the purity of the styrene, and the additives which were deliberately used in the reaction of the radiated PE film with styrene. The graft percentage was 20–220%. (ii) The PE/PS films were treated with hot concentrated sulphuric acid. Increase in the weight of the films showed that sulphonation had taken place. In control experiments, where ungrafted PE films were treated with sulphuric acid, the weight of the films was unchanged. These results imply that the sulphonation took place exclusively on the grafted styrene, yielding polystyrene-sulphonic acid (PSSA). The degree of sulphonation was usually 100–120% of the amount of PS in the films, implying complete mono-sulphonation of the aromatic rings in the film. The capacity of the films could be expressed as mequiv./g, combining the percentage of grafting and sulphonation. Films having 2–5 mequiv./g were prepared.

The polymerization of pyrrole inside the PE/PSSA was carried out in a two-compartment, three-electrode cell. A salt bridge (Agar) was used to connect the anodic and cathodic half-cells. The catholyte was 1 M aqueous FeCl<sub>3</sub>, with a carbon

rod as the cathode. The anolyte was 10 mM aqueous FeCl<sub>3</sub>, and a large-area Pt electrode served as the working electrode. In some experiments, supporting electrolyte was added to the anolyte. In a typical experiment, after assembly of the cell, the anolyte was stirred and the system cooled to 2 ± 2°C. A constant potential of 550 mV (vs. standard calomel electrode, SCE) was applied to the working electrode and the system was allowed to reach a steady state (constant minimum current). Several round pieces (radius 0.6 cm) of PE/PSSA (4.56 mequiv./g) were placed in the anodic compartment. The films immediately became reddish, as iron(III) diffused into the film exchanging the protons of the styrene-sulphonic acid. The incorporation of iron(III) ions into the films was also confirmed by a decrease in the peak height of the iron(III)/iron(II) wave in a cyclic voltammetry run, after the addition of the PE/PSSA films to the solution. After a steady state had been attained, pyrrole was injected into the anodic compartment to a concentration of 80 mM. The ratio of iron(III)/pyrrole was 0.125. Initially (~ minutes) the films gradually became black as PPy was formed in the films, while the solution remained colourless. Samples of the ionomer were removed at intervals and washed by soaking in 1 M aqueous HCl for 15 h,<sup>8</sup> after which they were dried and their conductivity was measured using the four-probe Van der Pauw technique.<sup>9</sup> During the polymerization of pyrrole in the induced chemical-electrochemical process the film thickness did not change. The thickness was measured with a digimatic bench micrometer having a resolution of 1 μm.

A typical variation of film conductivity with reaction time is shown in Figure 1. After 1 h a conductivity of 5–10 S cm<sup>-1</sup> was obtained. The conductivity increased and reached a constant value after 4–5 h. The final conductivity depended upon the temperature of the reaction; higher conductivities were achieved at lower temperatures (33 and 18 S cm<sup>-1</sup> at 2 and 25°C, respectively).

The addition of an electrolyte to the electrochemical reaction mixture increased the formation of undesired PPy powder in the solution and on the electrode. When 1 M NaCl was used as a supporting electrolyte, a black precipitate (pyrrole black) appeared after 5 min. Formation of PPy powder in the solution was prevented by the use of a low concentration of NaCl. Thus, with [NaCl] < 0.05 M only PE/PSSA/PPy was obtained in the process (4.5 h). The supporting electrolyte shortened the time required to reach

the maximum conductivity, but had almost no effect on its absolute value. Conductivities of  $30 \text{ S cm}^{-1}$  were obtained after 345 and 290 min when concentrations of 0 and 0.05 M NaCl were used, respectively. A somewhat better conductivity ( $38 \text{ S cm}^{-1}$ ) was obtained when 0.05 M toluene-*p*-sulphonic acid was used as the electrolyte.

During the experiment a constant potential was applied to the working electrode (potentiostatic process). According to the Nernst equation this potential should determine the ratio between the oxidized and reduced states of the iron couple and, thereby, the oxidative strength of the system can be controlled. Surprisingly it was found that similar conductivities were obtained regardless of the applied potential (between 450 and 600 mV). Moreover, similar times were required to achieve the maximum conductivity (Figure 2). Below 450 mV only a low conductivity was achieved, even after a long time. The high tendency of iron(III) to exchange protons in the ionomer resulted in films in which the loading of iron(III) ions was independent of the iron(III)/iron(II) ratio in the solution. Similar contents of iron(III) in the ionomer, regardless of the applied potential, might have caused similar conductivity after similar reaction times. These results show the importance of the first stages in the polymerization; although the maximum conductivity was achieved after 4–5 h it was governed by the initial content of iron(III) in the film. It should be noted that a control experiment, under open-cell conditions, yielded films with very low conductivity ( $<10^{-5} \text{ S cm}^{-1}$ ).

In summary, a new concept for the preparation of conducting polymers is presented. Chemical and electrochemical processes are combined to form conducting polymers catalytically.<sup>10</sup> This new process was utilized to form polypyrrole-based conducting ionomers with conductivities of 30–40  $\text{S cm}^{-1}$ . The composition, structure, and mechanical proper-

ties of these conducting ionomers are being investigated, and this process is being extended to the preparation of other conducting polymer composites.

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