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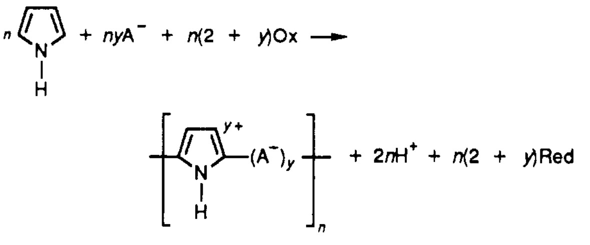
Stoichiometry and Kinetics of Pyrrole Polymerization

Introduction. Numerous electrically conductive polymers, such as the polypyrroles and the polyanilines, are currently produced by heterogeneous oxidative polymerization of monomer in aqueous solution.[1,2] The process involves a soluble oxidizing agent, Ox, which is converted to its reduced form, Red, on reaction with the monomer, as illustrated by the polymerization of pyrrole·



(1)

where A is a counteranion from the reaction mixture. Usually, two electrons are required to couple each monomer, and a further fractional charge, *y*, provides the charge carriers that impart electrical conductivity to the material. The polymer can also be produced in smaller amounts by electrochemical polymerization,[3] where the number of electrons consumed is determined via coulometry, and the consumption of monomer can be measured by in situ weight gain of the electrode.[4] Determining the overall reaction stoichiometry for heterogeneous solution polymerization is not straightforward, since many analytical techniques are rendered ineffective by the increasing opacity of the solution, which contains suspended conducting polymer particles. Thus, while the properties and composition of the final polymer are well-known, little information exists as to the kinetics and reaction pathway.

Since the reaction is promoted by oxidation, it should be possible to use potentiometry to monitor consumption of Ox, using the Nernst equation:

$$E = E^{\circ\prime} + \frac{RT}{nF} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Red}]} \tag{2}$$

Indeed, in situ potentiometry has been used to follow the course of pyrrole[5] and aniline[6] polymerizations. Although this technique is easily implemented, it does not measure the monomer used, and assumptions must be made regarding stoichiometry throughout the reaction. Our objectives in the present work were to provide an independent method to confirm the utility and limitations of potentiometry and to measure each component of the reaction mixture in situ.

Experimental Procedures. Ferricyanide ion, $Fe(CN)_6^{3-}$, was used as the oxidizing agent, which yields ferrocyanide, $Fe(CN)_6^{4-}$, as a result of a one-electron oxidation. Polymerizations were carried out at room temperature in aqueous solution using 0.075 M pyrrole and 0.30 M potassium ferricyanide (a 4:1 mole ratio of oxidant/monomer). Typically, 100 mL of pyrrole solution and 14 g of Na_2SO_4 were placed in a stoppered 250-mL Pyrex conical flask, and 100 mL of potassium ferricyanide solution was added to the system with continuous stirring. A thin film of polymer which formed on the surface of the container was removed with the aid of a Teflon stirbar wrapped with glass wool. The fiber-optic-based Raman system consisted of a Coherent Innova 70 argon ion laser (514 nm) typically operating at 560 mW, a Jobin Yvon HR-640 monochromator, a notch filter (Omega Optical Inc.), and a Tracor-Northern TN 6100 intensified diode-array detector interfaced to a microcomputer. The entrance slit was 400 μm, giving a spectral resolution of 10 cm^{-1}. Incident radiation was passed via the central core of a 200-μm multimode step index fused-silica fiber-optic bundle, 1 m long (General Fiber Optics Inc.). Scattered radiation was collected by the six outer fibers of the same bundle. To record spectra, the end of the fiber was simply placed against the wall of the container. Signal averaging was allowed for a period of 1 min. In order to correct for decreasing scattering volumes as the polymerization progressed, sulfate ion was added as an internal standard. As shown in Figure 1, signals for all species were well-resolved. Raman shift frequencies used for detection of monomer, ferrocyanide, ferricyanide, and sodium sulfate internal standard were 1147, 2058/2094, 2133, and 982 cm^{-1}, respectively. No significant signal was observed from solution-dispersed polypyrrole particles. Values for concentrations were calculated using least-squares fitting of data. Using the conditions stated the detection limit for ferricyanide/ferrocyanide was approximately 0.1 wt %. Precision for an equimolar mixture of a 0.15 M mixture of ferricyanide/ferrocyanide was experimentally determined to be ±0.17%, and accuracy was better than ±2%. More extensive details of the experimental setup and data treatment are described in a separate publication.[7] Potentiometry was performed with a Pt wire indicating electrode, referenced to saturated calomel, and an electrometer. The formal potential, $E^{\circ\prime}$, for the ferricyanide/ferrocyanide couple under the conditions used was determined by measuring the potential of an equimolar mixture of ferro- and ferricyanide.

Results and Discussion. One of the advantages of scattering techniques is that the requirements for good optical clarity of the sample are removed. Raman spectroscopy is ideal for work in aqueous solutions due to weak Raman scattering from water molecules. In the present system, all peaks, including the ferro- and ferricyanide C≡N stretching, were well-resolved. Few interferences from polypyrrole or silica background, both of which were broad and easily subtracted, were observed. The use of a sealed system allowed us to maintain careful material balance throughout the reaction. During polymerization the decrease in the ferricyanide peak intensity was matched by an increase in the ferrocyanide signal. The electrical conductivity of the polypyrrole, measured by the four-probe technique on pressed pellets of dried powder, was 5.3 Ω^{-1} cm^{-1}.

In Figure 2 the raw potentiometric data vs time are presented. Also depicted in Figure 2 is the amount of ferricyanide consumed calculated from eq 2, and also measured simultaneously by Raman scattering. Good agreement between the two techniques as to the disappearance of ferricyanide is obtained over this time scale. Some divergence between the two methods is seen at longer times due, possibly, to film formation on the electrode or clogging of the reference electrode junction with polymer. For example, at 2500 min the amount of oxidant consumed from potentiometry is 22% less than the amount determined from Raman measurements. Since agreement is good at short time, we are confident that potentiometry can be used to probe nucleation processes that presumably occur at the beginning of the polymerization. Interestingly, we see no difference in polymerization kinetics when a stabilizer such as poly(vinyl alcohol) (2 wt %) is included in the initial mixture. Armes[8,9] has shown that stabilizers can be used to promote the formation of easily identified individual colloidal particles of polymer. It appears that

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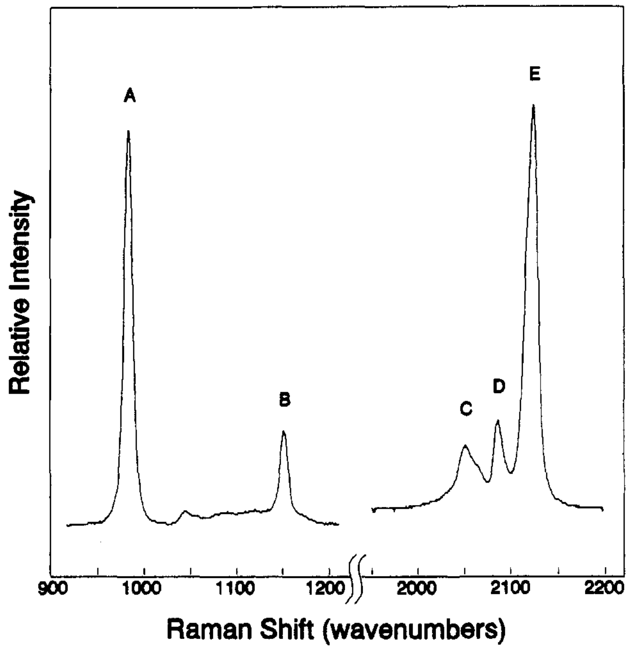

Figure 1. Raman spectrum of a polymerizing solution of ferricyanide and pyrrole in water. Peak A is from sulfate internal standard, peak B is from pyrrole, peaks C and D are ferrocyanide bands, and peak E is from ferricyanide. The relative intensities of two windows corresponding to two positions of the 1024-pixel diode-array detector are shown.

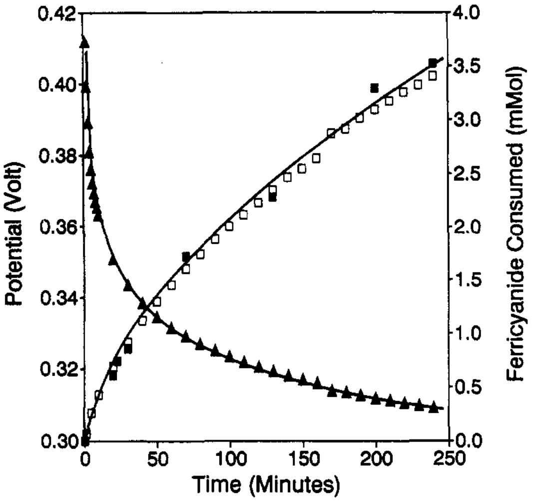

Figure 2. Electrode potential vs time and ferricyanide consumption vs time determined from potentiometry (□) and from Raman scattering (■) for polymerization of 200 mL of 0.075 M pyrrole in water.

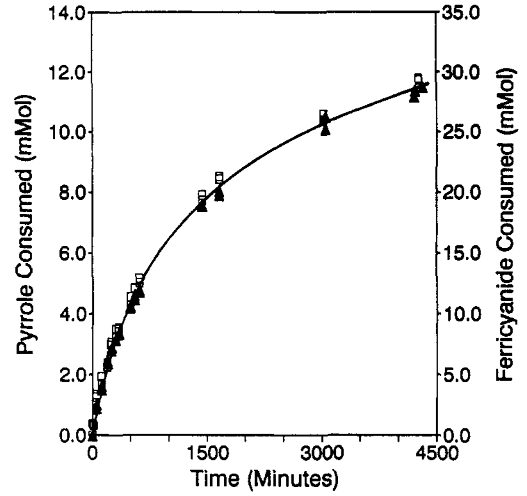

Figure 3. Pyrrole monomer (□) and ferricyanide (▲) consumed as a function of polymerization time determined in situ by Raman scattering.

coatings of stabilizer are not dense enough to affect the rate of polymerization.

To determine the overall composition of the polymer, it is possible to perform elemental analysis at various time intervals. However, this approach is laborious, and access to early regimes of the polymerization is limited by the requirement for sufficient sample to analyze. Figure 3, depicting both pyrrole and oxidizer consumption as a function of time, illustrates that the reaction may be monitored in situ by Raman scattering over a wide range of conversions (after 4500 min 80% of the monomer has been converted to polymer). The axes for pyrrole and ferricyanide have been scaled by a ratio 1:2.5, respectively. Coincidence of data points over all times indicates that the reaction stoichiometry is 1 to 2.5 for the entire polymerization. This result contrasts with the findings on aniline polymerization of MacDiarmid et al.,[10] who note, after quenching the reaction and analyzing the polymer, that polyaniline is first produced in a highly oxidized form when peroxydisulfate is used as oxidizer. Polyaniline can be obtained in a variety of protonation/oxidation states: in particular, the fully oxidized ($y = 1$) form of polyaniline may be obtained with strong oxidizing agents, in contrast to polypyrrole, which cannot be produced in such a high oxidation state and which does not have as rich an acid/base chemistry as polyaniline. The ferricyanide oxidizing agent we use in our experiments is rather mild. It takes ca 3 min before the solution becomes visibly opaque. If a stronger oxidizing agent, such as ferric chloride ($E° = 0.77$ V), is added to our system, other parameters remaining the same, the solution turns black right away. The choice of a mild oxidizing agent, leading to slower polymerization, was necessitated by the minimum time resolution of 1 min to record a spectrum. This limitation underscores the advantages of the potentiometric method, since the resolution is less than 1 s and the very beginning of the polymerization, where one would expect nucleation to predominate, can be monitored.

The polypyrrole resulting from the reaction described can be expected to contain a mixture of dopant ions, including sulfate and ferri- and ferrocyanide. The use of a nonionic internal standard, which is presently being pursued, would simplify the composition of the polymer. Elemental analysis was performed on polymer collected at the end of a polymerization, washed with deionized distilled water, and dried under vacuum at 50 °C. Iron was measured either by atomic absorption of polypyrrole solubilized by digestion with bleach or by gravimetric analysis (samples were heated in air at 950 °C to constant weight, and Fe was determined as Fe_2O_3). Results were as follows (%): C, 53.4 (53.8); H, 3.9 (3.2); N, 18.2 (18.3); S, 2.2 (2.2); Fe, 2.32 (2.45) (calculated for $[(C_4H_3N)(Fe(CN)_6{}^{3/4-})_{0.04}(SO_4{}^{2-})_{0.07}]_n$ and 15% water content[11]). The actual doping level depends on the speciation of the iron as ferri- (three charges) or ferrocyanide (four charges), which is information that elemental analysis cannot provide. For ferrocyanide-containing polymer the doping level would be 0.28 charges per pyrrole, and for ferricyanide y would be 0.25.

The measured stoichiometry of 2.5:1 from Figure 3 implies the doping level, y in $[(C_4H_3N)(A^-)_y]_n$, is 0.5. This value is higher than that obtained from the elemental analysis and from electrochemical methods (ca. 0.4[11]) but must be corrected, since the polymer contains 4.3 mol %

ferro- and/or ferricyanide, as determined above. Any ferrocyanide/ferricyanide incorporated into the polymer is not observed in the Raman experiment (as indicated by the absence of ferro- and ferricyanide bands from Raman spectra of polypyrrole powder). This provides the opportunity to determine the species of the iron-containing dopant ion. If ferricyanide is the dopant ion, the apparent extent of reaction measured by Raman scattering is too large, and the converse is true if ferrocyanide is the dopant ion. The corrected doping level from the Raman experiment would be 0.38 if the polymer contained ferricyanide and 0.66 if it were doped with ferrocyanide. Since the former value is closer to that obtained by elemental analysis, we believe the dopant ion to be ferricyanide.

Conclusions. Raman scattering is a versatile technique for the in situ analysis of highly absorbing heterogeneous suspensions of polypyrrole. Quantitation of monomer, oxidizer, and reduced product is possible. The method will be particularly useful for monitoring the progress of composite formation, for example, the coating of latex particles or other fillers with conductive polymers.[12-14] We are currently exploring the utility of the technique for other conducting polymers, such as the polyanilines, and for nonaqueous polymerization media.

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Joseph B. Schlenoff,* Yoke Fong, and Chengbo Shen

Department of Chemistry and
Center for Materials Research and Technology
Florida State University, Tallahassee, Florida 32306

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Registry No. Pyrrole, 109-97-7; polypyrrole, 13746-66-2; potassium ferricyanide, 30604-81-0.