Electrochemically Prepared Polypyrroles
from Aqueous Solutions

Renyuan QIAN and Jinjin QIU

Institute of Chemistry, Academia Sinica, Beijing, China

ABSTRACT: Polypyrrole (PPy) films generated electrochemically from aqueous solutions have been found to have also good electrical conductivity. PPy films with the counter anions TsO^-, $SO_4^=$, and NO_3^- showed compact structure with apparent densities close to their flotation densities. The oxidative stability of PPy films has been compared by the value of the oxidation peak E_{pa} around 1.0 V (*vs.* SCE) in the cyclovoltammogram. Prolonged electrolysis at $+0.8$ V led to oxidative degradation. The temperature dependence of the conductivity followed the variable range hopping equation. However voltage shorted compaction (VSC) conductivity measurements might show pronounced differences at low temperatures for some of these films. No significant frequency dependence of the conductivity was found up to 35 GHz. In the IR spectra of electrochemically reduced PPy film by transmission the v (N–H) and sp^2 v (C–H) absorption bands were observed with no sp^3 v (C–H) bands. On grinding the reduced film with KBr to make powder compact the sp^3 v (C–H) absorption bands appeared indicating a mobile proton on the N-atom of the pyrrole ring. Definite evidence from IR spectra for the de-intercalation of the counter anion of the conducting PPy film during electrochemical reduction and chemical compensation has been obtained. The intercalation and de-intercalation of the counter anions was found to be accompanied by profound morphological changes. Molecular composites from *in situ* polymerization of aqueous pyrrole solution in a flexible polymer are briefly discussed.
  KEY WORDS Conducting Polymer / Polypyrrole / Electrochemical Polymerization / Morphology / Chain Structure / Intercalation /

Although Dall'Olio *et al.*[1] electrochemically polymerized pyrrole in aqueous H_2SO_4 even long before conducting polymers became of wide interest, conducting polypyrrole (PPy) have usually been prepared from acetonitrile solution.[2] Recently it was found that pyrrole could be electrochemically polymerized and intercalated in aqueous solution with various types of counter anions to give PPy films of good conductivity, including detergent anions as *n*-alkyl sulfates, sulfonates,[3] alkyl aryl sulfonates,[4] tosylate anion,[4] and polymeric anions as polyvinyl sulfate and polystyrene sulfonate,[5] polymethacrylate, and sulfonated polyvinyl alcohol[6] as the counter anion. In our laboratory we found that with $SO_4^=$, NO_3^-, and TsO^- as the counter anions we can get com-

pact conducting PPy films containing less than 20% void volume, other counter anions gave films of 70—85% void.[7,8] In this paper results of our recent investigation[9] on these dense conducting PPy films are summarized including morphology, oxidative stability, metallic conduction, chain structure, deintercalation and re-intercalation of the counter anions. A brief account for the molecular composites containing PPy is also given.

MORPHOLOGY AND DENSITY

Conducting PPy films with ClO_4^-, BF_4^-, and PF_6^- as the counter anion show a morphology of hollow bowls of 20—30 μm diameter and consequently have very low apparent density
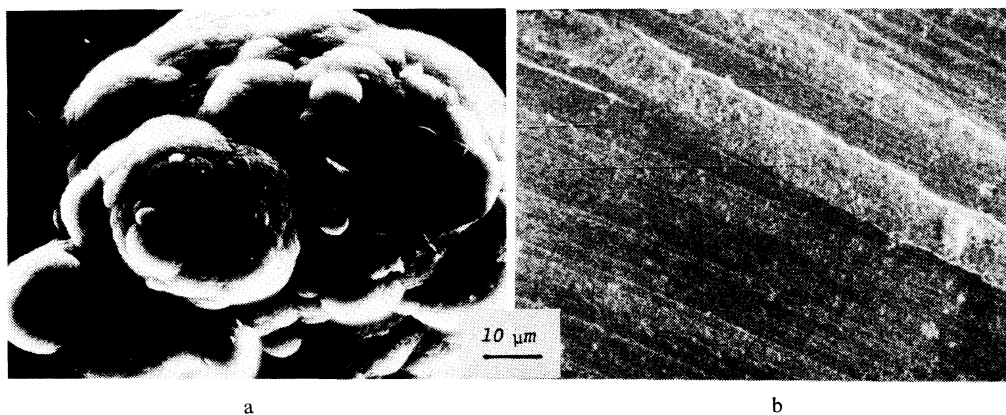
Figure 1. SEM photographs of TsO⁻ intercalated PPy film. a, facing the electrolyte; b, facing the Pt electrode.
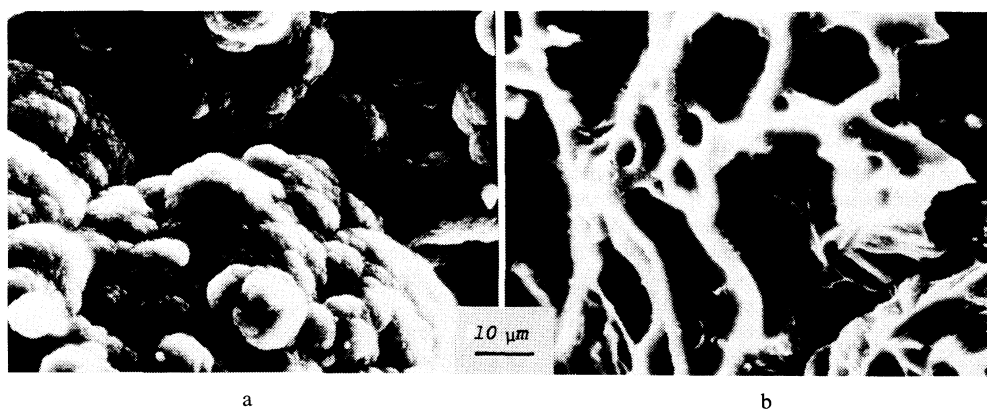

Figure 2. SEM photographs of ClO_4^- intercalated PPy film. a, facing the electrolyte; b, facing the Pt electrode.
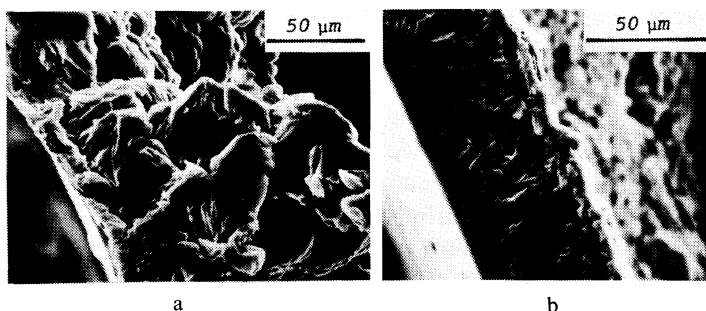

Figure 3. SEM photographs of the fracture surface of (a) TsO⁻ (b) $SO_4^=$ intercalated PPy films.

as calculated from the dimensions and mass of the film electrochemically prepared either from acetonitrile solution or from aqueous solution.[7] The morphology is controlled by the nature of the counter anion rather than the nature of the solvent used in electrolysis. The contrast of the morphology of TsO⁻ intercalated PPy film against that of ClO_4^- interca-

158

Table I. Densities of anion intercalated PPy films at 20.0°C prepared
electrochemically from aqueous solutions

Supporting electrolyte	$S\,cm^{-1}$	Flotation density $g\,cm^{-3}$	Apparent density $g\,cm^{-3}$	% void[a]
HClO$_4$	20—30	1.575	0.52	67
NaClO$_4$	—	1.558	0.36	77
NaBF$_4$	12	1.540	0.38	73
KPF$_6$	12	1.549	0.46	70
TsOH	60—200	1.368	1.24	9
TsONa	60—200	1.364	1.25	8
NaNO$_3$	4—30	1.516	1.25	18
H$_2$SO$_4$	10	1.532 (1.514[b])	1.26 (1.50[b])	18 (1[b])
Na$_2$SO$_4$	15—20	1.524	1.27	17
KCl	46	—	—	—
KBr	21	—	—	—
K$_3$Fe(CN)$_6$	19	—	—	—

[a] Calculated from flotation and apparent densities.
[b] Another set of data.[7]

lated one is shown in Figures 1 and 2. They are both constructed of 1 μm or less diameter particles aggregated into the form of a califlower but the former is densely packed while the latter is hollow as easily seen from the film surface facing the Pt electrode used in electrolysis. In the former case the surface facing the electrode is smooth enough to reproduce the surface scratches on the electrode surface. The film polymerized in Na$_2$SO$_4$ is even more compact than that polymerized in TsONa as revealed in the SEM photographs of the fracture surfaces shown in Figure 3.

The flotation density determined at 20.0°C in a density gradient column made of 1,2-dibromoethane/hexane mixtures of density values 1.40 and 1.70 g cm^{-3} and the apparent density calculated from the area and thickness and the mass of the film are listed in Table I for PPy films of various counter anions prepared from aqueous solutions. The TsO$^-$ intercalated PPy film has smaller flotation density than other anion intercalated PPy, presumably due to the length of the non-spherical TsO$^-$ ion.

OXIDATIVE STABILITY

When an intercalated PPy film is put into the same supporting electrolyte solution as the film was electrochemically generated and cyclovotammogram is run, an oxidation peak will be observed on the first scant at E_{pa} values around 1 V vs. SCE depending on the intercalated anion.[10] The peak current i_{pa} has been found to be proportional to the value of mC cm^{-2} from which the intercalated PPy film was made. No reduction peak could be identified during the back scan, and on the second scan cycle the oxidation peak current becomes very small and E_{pa} shifts to lower values. The oxidation peak will vanish completely on subsequent scans. These facts indicate that an irreversible oxidation is occurring during the cyclovoltammetry beyond +1 V. Similar conclusion was arrived by Asavapiriyanont[11] using KNO$_3$ as the supporting electrolyte. The values of E_{pa} for intercalated PPy films of 10 mC cm^{-2} made from TsOH, TsONa, H$_2$SO$_4$, and Na$_2$SO$_4$ solutions are 1.13, 0.99, 1.07, and 0.96 V respectively at a potential scan rate of 50 mV s^{-1}. When TsO$^-$, NO$_3^-$, and
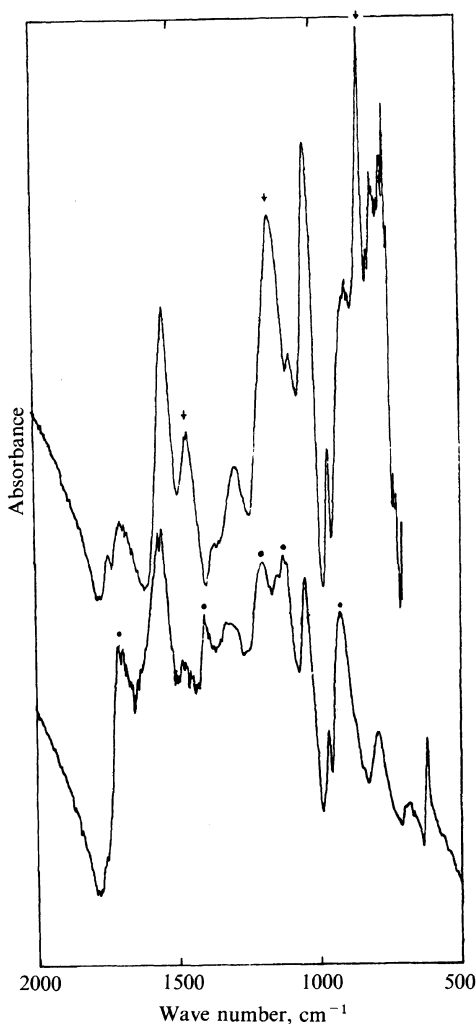
Figure 4. IR spectrum of a $SO_4^=$ intercalated PPy film maintained in Na_2SO_4 solution at $+0.8$ V vs. SCE for 2 h (lower curve) as compared to that of an ordinary $SO_4^=$ intercalated PPy film (upper curve). Dots indicate the new bands or bands with enhanced intensity. Arrows indicate bands with reduced intensity in the lower curve.

$SO_4^=$ intercalated PPy films are put into aqueous solutions of their corresponding electrolytes and a constant potential of 0.8 V is applied for a duration of 1—2 h, the films will become brittle with their conductivities being dropped significantly and the solutions turn to pink to brown, presumably due to the presence of oligomers disintegrated from the film during the oxidation process. The IR spectrum of a
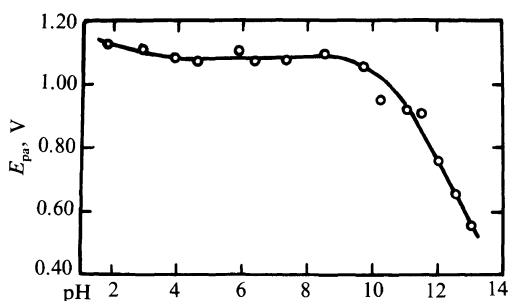

Figure 5. Effect of pH of the solution containing 0.1 M TsO^- ion on the value of E_{pa} of cyclovoltammogram of TsO^- intercalated PPy film.

$SO_4^=$ intercalated PPy film polymerized from Na_2SO_4 solution maintained at 0.8 V for 2 h is shown in Figure 4. As compared to the spectrum of usual $SO_4^=$ intercalated PPy film the intensities of the absorption bands at 1466 and $1178 \, cm^{-1}$ are very much reduced, while the absorption band at $1697 \, cm^{-1}$, which is $v(C=O)$ absorption in the oxidized product, is much enhanced and new bands at 1198 and $1117 \, cm^{-1}$ appear with considerable intensities. Thus we are quite sure that the electrochemical oxidation peak E_{pa} around 1 V leads to chemical oxidation accompanied by some degradation of the PPy chain. This E_{pa} value could be considered as a criterion for oxidative stability of the intercalated PPy film, lower E_{pa} values indicating less oxidative stability. So, for the same intercalated anion the PPy film made in a neutral solution has lower oxidative stability than that made in an acid solution.

For accessing some idea about the relative oxidative stability of conducting PPy in solutions of various pH values a TsO^- intercalated PPy film of $10 \, mC \, cm^{-2}$ is put into a 0.1 M TsOH solution with the solution pH adjusted by means of Britton–Robinson buffer (pH 1.5—12) or adding NaOH solution (pH > 12) and the cyclovoltammogram is run on the first scan at $50 \, mV \, s^{-1}$. The E_{pa} values obtained[8] in solutions of pH 1.5 to 13 are shown in Figure 5. Evidently the TsO^- intercalated PPy film has good oxidative stability
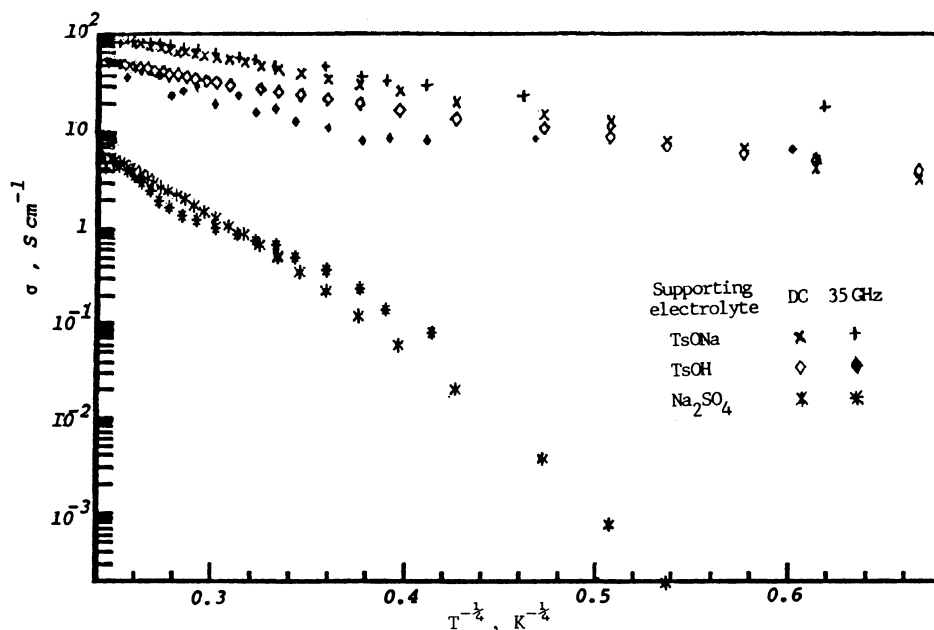
Figure 6. Temperature dependence of the conductivities of intercalated PPy films.

in acidic and neutral solutions while the stability deteriorated steadily beyond pH 9. Similar results are observed with $SO_4^=$ intercalated PPy film.

THE METALLIC CONDUCTIVITY

All conducting polymers show a decrease in conductivity with decreasing temperature characteristic of a semi-conductor when measured by the ordinary 4-probe method. In most cases the conductivity–temperature relationship follows closely the so called variable range hopping relation[12] over rather wide temperature ranges:

$$\log(\sigma T^{1/2}) = A - BT^{-1/4}$$

Thus a plot of $\log(\sigma T^{1/2})$ or simply $\log \sigma$ vs. $T^{-1/4}$ gives a straight line as shown in Figure 6 for intercalated PPy films prepared from aqueous solutions.[13] Also shown in the figure is the frequency independence of the conductivity behavior from DC to 35 GHz in the microwave region.

The only direct evidence for metallic conduction for PPy and conducting polymers in general comes from the thermopower measurements. The Seebeck coefficient S at low temperatures is proportional to the absolute temperature passing through the origin on S–T plot, the value of S being a few $\mu V\,K^{-1}$, typical of metals, as shown in Figure 7 for the same samples as in Figure 6. For organic semi-conductors the value of S lies between 10^2—$10^3\,\mu V\,K^{-1}$. For some time we have suggested that in ordinary 4-probe conductivity measurement the conductivity behavior observed is masked by the intergranular or interfibrillar contact resistance because of the heterogeneous morphological structure of the conducting polymers. We adopted the voltage-shorted compaction (VSC) method of conductivity measurement for polycrystalline powder compactions[14,15] to conducting polymers.[16,17] VSC conductivity data do actually show an increase of conductivity with decreasing temperature typical of metals, as shown in Figure 8 for TsO⁻,
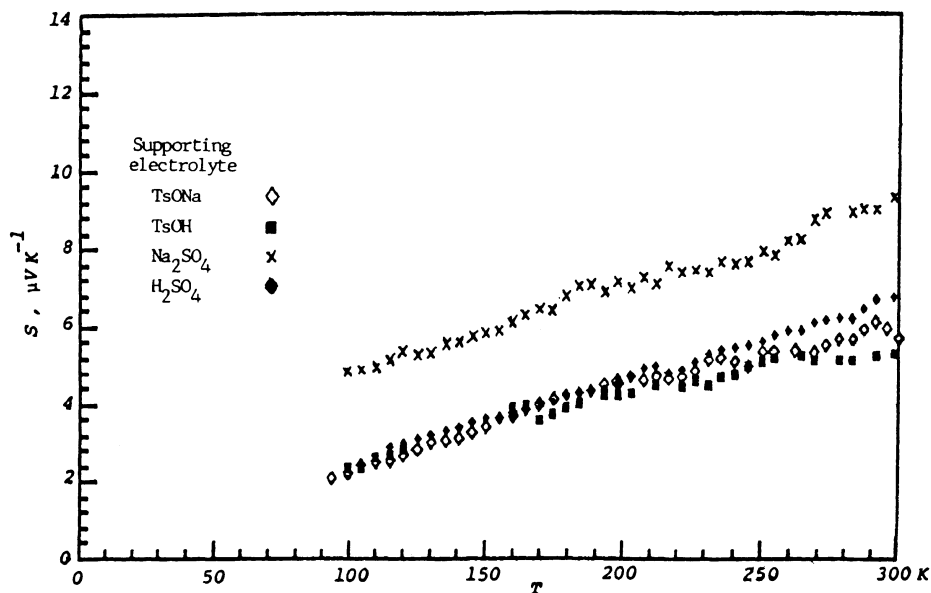
Figure 7. Temperature dependence of the Seebeck coefficients of intercalated PPy films.
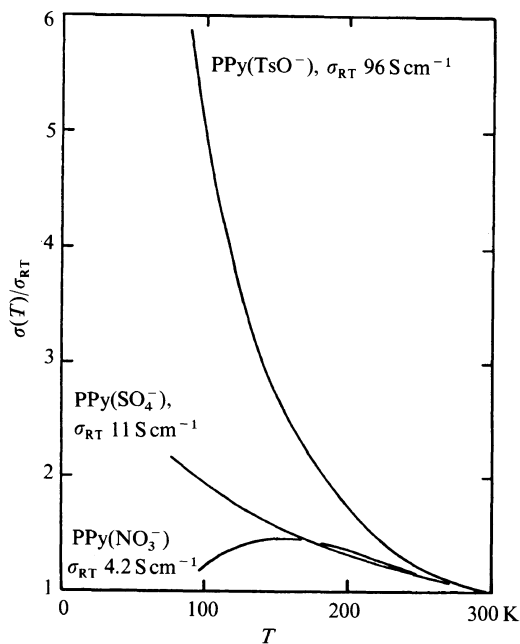

Figure 8. VSC curves of the intercalated PPy films.

$SO_4^=$, and NO_3^- intercalated PPy films.[8] PPy films of higher room temperature conductivity usually show a more pronounced increase of conductivity with decreasing temperature. PPy films of lower conductivity in some cases show a broad maximum at low temperature,[8,17] although no much difference in conductivity behavior could be detected at all by 4-probe measurements. We believe that VSC measurement can actually reveal some aspects of the intrinsic conductivity behavior of conducting polymers. In view of such considerations the intrinsic conductivity of conducting polymers must be very much higher than the values we now usually assume from 4-probe measurements. In VSC measurement the specimen between two voltage measuring terminals is short circuited by a thin coating of Ag paste, so the absolute value of conductivity of the sample can no longer be evaluated while the temperature dependence of its conductivity is reflected in the VSC curve observed as a closer analysis of the situation has shown.[15] In applying Ag paste to the specimen it must be very careful so that the Ag coating on the surface must be very thin yet the paste penetrates into the specimen to some depth.

CHEMICAL STRUCTURE OF PPy CHAIN

The pyrrole units in a PPy chain are mainly α,α'-linked from the evidence obtained in IR[2] and solid state NMR.[18] The mol mass and its distribution are so far inaccessible experimently because of its insolubility. Some puzzling facts about the chemical structure of PPy chain remain not understood.

Elemental analysis of intercalated PPy always shows an excess of H in the mol ratios C:H:N and a considerable amount of O in the sample as shown in Table II. The amount of O content in the sample cannot be simply attributed to oxidation to form $C=O$ groups which would give a strong IR absorption band around $1700 \, cm^{-1}$. In the IR spectra of PPy films, however, only weak absorption is observed, and in the cases of PPy from $NaNO_3$, TsONa, and $K_3Fe(CN)_6$, for example, v $(C=O)$ absorption is barely noticeable as shown in Figure 9. We suppose that O in conducting PPy is mainly present in the form of charge transfer complex between O_2 molecules or atoms with the pyrrole units. It is also interesting to point out here that when $K_3Fe(CN)_6$ is used as the supporting electrolyte during electrochemical polymerization of pyrrole, the anion intercalated in the film is $Fe(CN)_6^{4-}$ instead of $Fe(CN)_6^{3-}$ as evident from the IR spectrum. During the charge transfer intercalation the counter anion is quite often reduced to lower valence state.

The excess amount of H could not be accounted for by the possible presence of pyrrolidone end groups as the oxidation product.[19] For intercalated PPy films because of rather intense IR absorption bands their IR spectra are usually taken on KBr powder compacts which show no v (N–H) and sp^2 v (C–H) absorptions while sp^3 v (C–H) absorption bands at 2850—$2940 \, cm^{-1}$ appear instead. For electrochemically reduced PPy films, which have conductivities usually less than $10^{-6} \, S \, cm^{-1}$, we have been able to get

Table II. Elemental analysis of intercalated PPy films electrochemically prepared from aqueous solutions, PPy^{y+} (yX^-)

Supporting electrolyte	C	:	H	:	N	:	y	:	O^a
TsOH	4		3.54		0.95		0.31		0.44
TsONa	4		3.44		1.00		0.31		0.40
H_2SO_4	4		3.35		0.97		0.19		0.68
Na_2SO_4	4		3.34		0.96		0.12		0.65
$NaNO_3$	4		3.24		1^b		0.19		0.84

[a] From balance.
[b] Assumed.

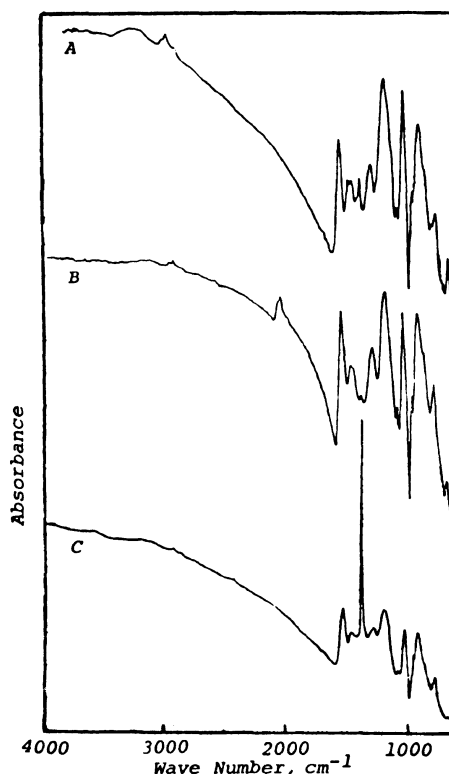**Figure 9.** IR spectra of TsO^- (A), $Fe(CN)_6^{4-}$ (B), and NO_3^- (C) intercalated PPy films by KBr powder compacts.

direct transmission IR measurement on thin films which show clearly the presence of v (N–H) band at $3450 \, cm^{-1}$ and sp^2 v (C–H) band at $3105 \, cm^{-1}$ and the absence of sp^3 v (C–H) absorption as shown in Figure 10. However, it is interesting enough that on
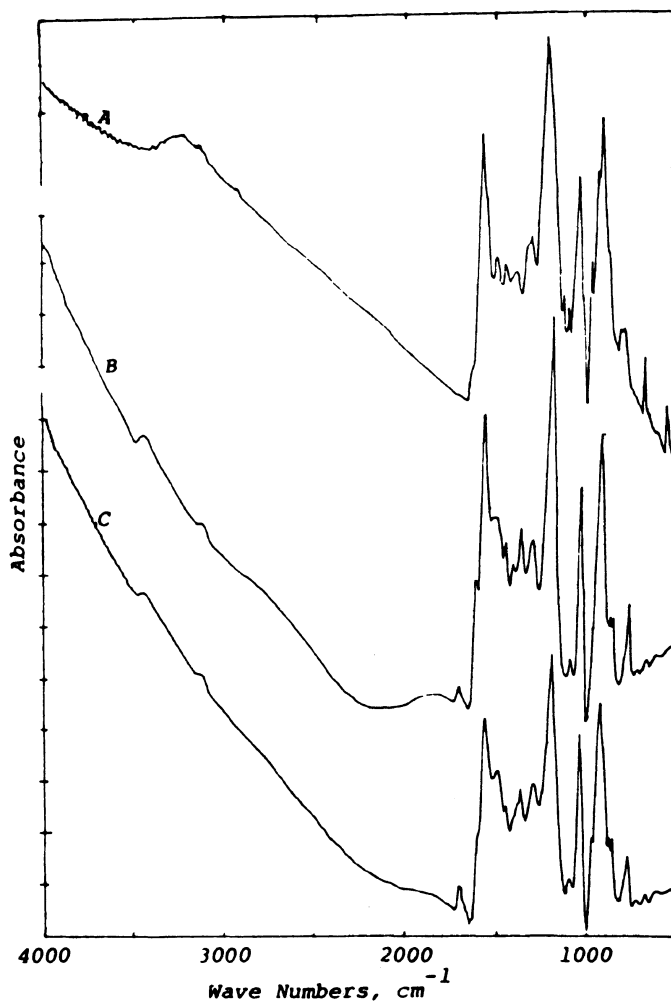
Figure 10. IR spectra of electrochemically reduced PPy films by transmission. A, from $SO_4^=$ intercalated PPy; B, from NO_3^- intercalated PPy; C, from TsO^- intercalated PPy.

grinding the reduced PPy film with KBr to make powder compact the sp^3 v (C–H) bands re-appear in its IR spectrum as shown in Figure 11. Presumably a charge transfer intercalation of Br^- takes place during grinding neutral PPy with KBr. This suggests a reversible structure change involving the mobile proton from N to β-C atom in the pyrrole unit during the charge transfer intercalation process:
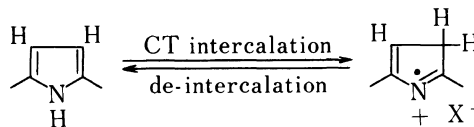
This reversible shift of H does not explain the excess H present in intercalated PPy films. At the moment it appears not clear from where the growing PPy chain picks up the excess H atoms, from the H atoms split off during anodic polymerization or from the solvent. To maintain a conjugated chain, as necessi-
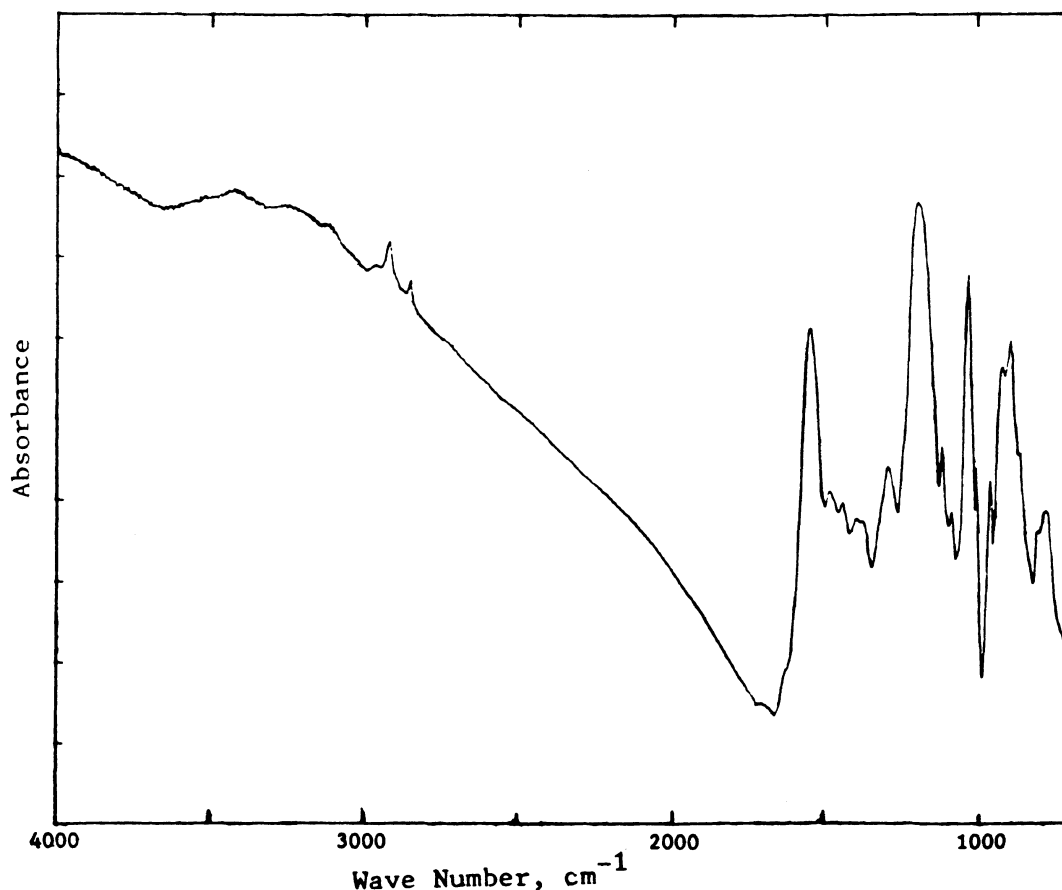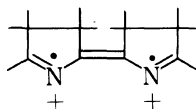
Figure 11. IR spectrum of KBr compact of an electrochemically reduced PPy from TsO⁻ intercalated PPy film.

tated by good conductivity, with more than 3H-atoms per pyrrole unit, a possible structure would involve the presence of the structural units of

This is however only a speculation. Further work has to be done.

DE-INTERCALATION AND RE-INTERCALATION

The terms "doping," "de-doping," and "compensation" were borrowed from semiconductor technology. The nature of these processes remains not entirely clear. We have taken the advantage of a very strong and sharp IR absorption band v (N–O) at $1384 \, \text{cm}^{-1}$ present in a NO_3^- intercalated PPy film to follow the electrochemical reduction and reoxidation processes and the chemical compensation process by NH_4OH or NaOH solution treatment. The electrochemically prepared PPy from $NaNO_3$ solution shows clearly the v (N–O) absorption band indicating the intercalated NO_3^- ion in the film. There have been reports of the absence of ClO_4^- absorption in PPy films prepared electrochemically from CH_3CN solution with Bu_4NClO_4 as sup-
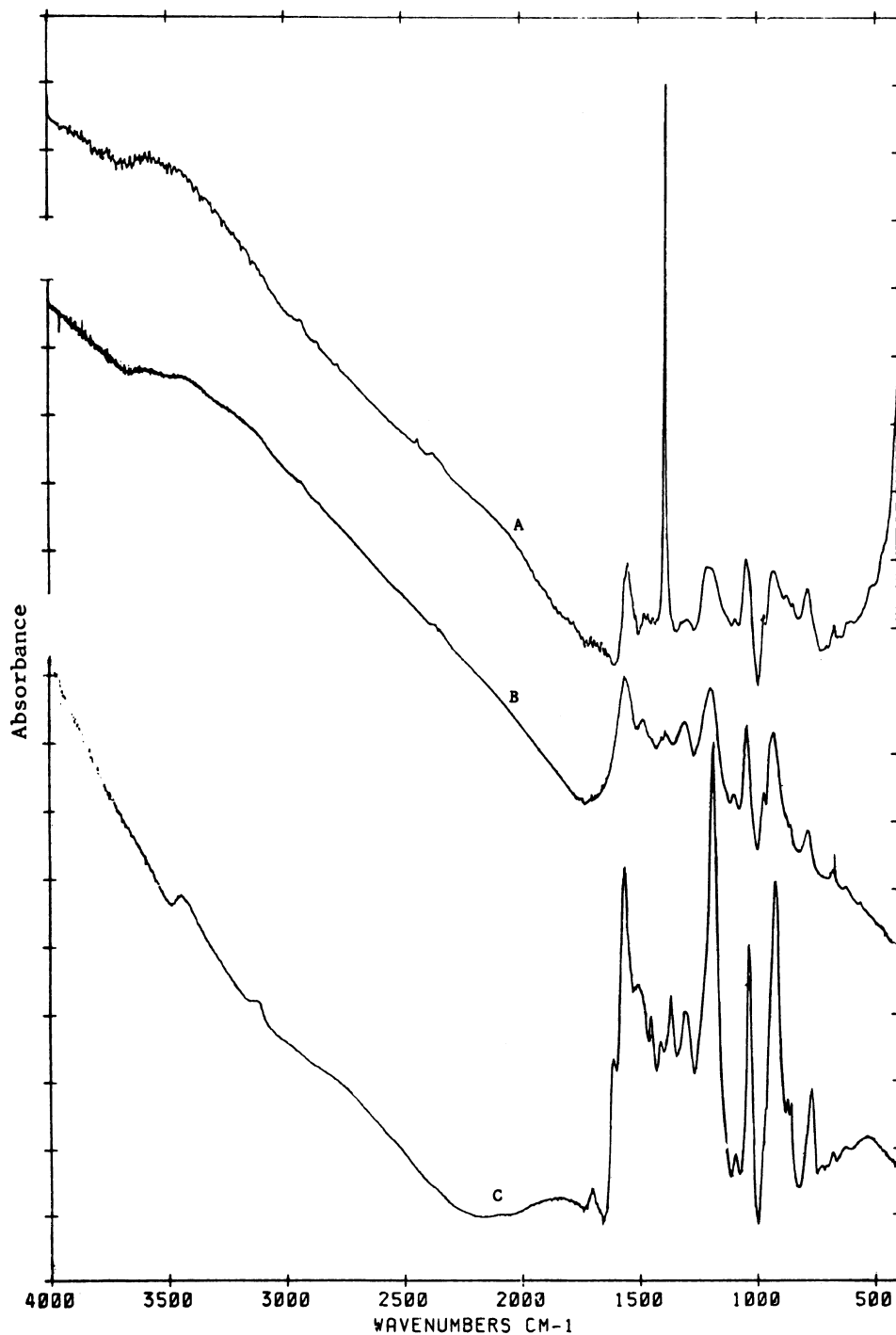
Figure 12. IR spectra of (A) NO_3^- intercalated PPy film; (B) the film A after treatment with 2 M NaOH solution for 6 h; (C) the film A after electrochemical reduction.

porting electrolyte.[20,21] However, ClO_4^- intercalated PPy film prepared in our laboratory from aqueous solution of $HClO_4$ or $LiClO_4$ does show the absorption bands at 627, 1120, and 1145 cm^{-1} attributed to ClO_4^- (*vide infra*).

When a NO_3^- intercalated PPy film is reduced electrochemically in a 0.1 M $NaNO_3$ solution at -0.8 V *vs.* SCE to a conductivity

of 10^{-6} S cm^{-1} or less, the reduced film gives much sharper and well resolved IR spectrum with no absorption at 1384 cm^{-1} as shown in Figure 12. This indicates clearly that the counter anion NO_3^- has been de-intercalated during the electrochemical reduction process. On the other hand when a TsO$^-$ intercalated PPy film is electrochemically reduced in a
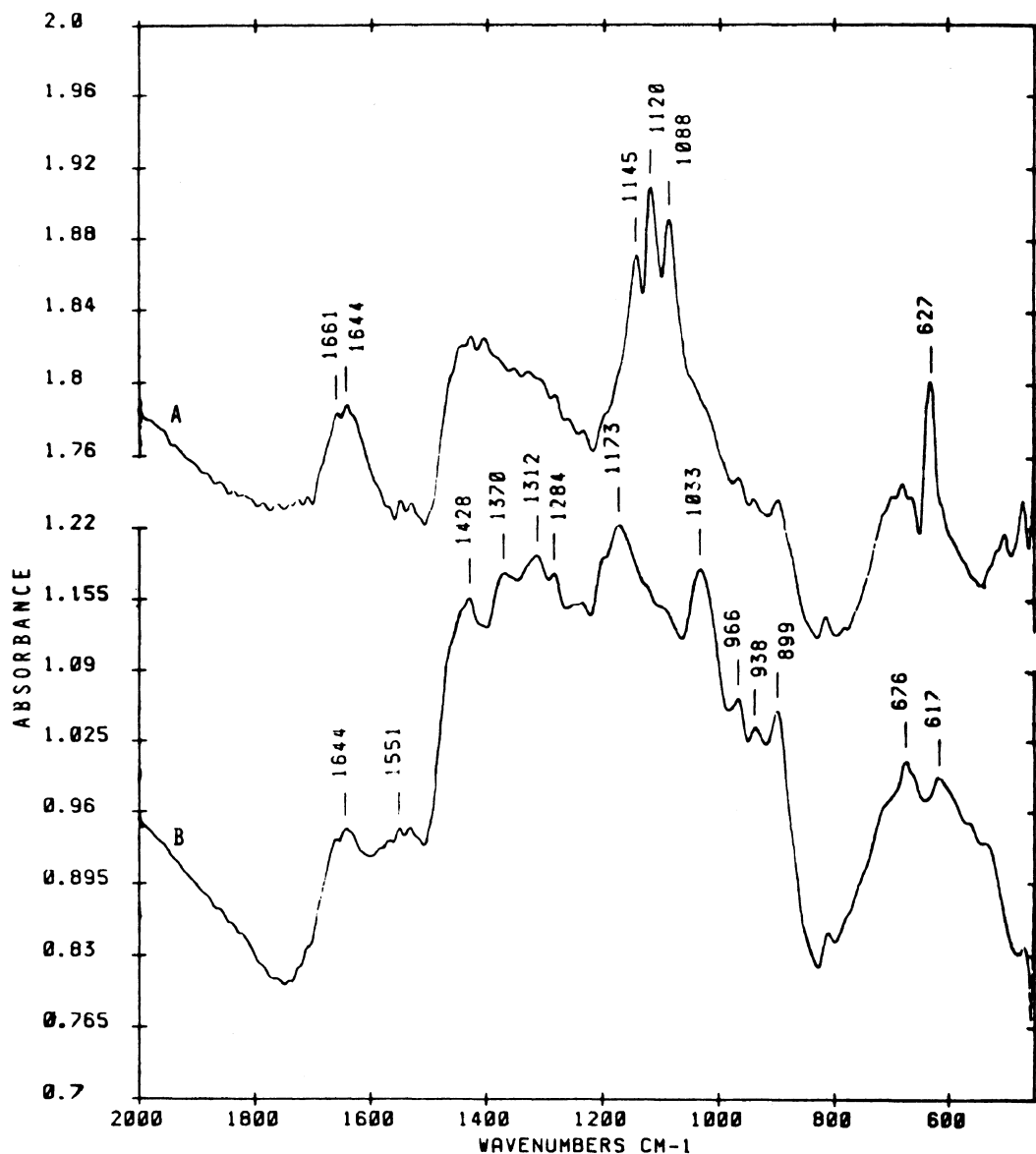

Figure 13. IR spectra of (A) a ClO_4^- intercalated PPy film; (B) the film A after electrochemical reduction.

0.1 M $NaNO_3$ solution and then re-oxidized electrochemically at $+0.4$ V $vs.$ SCE, the film after thorough washing shows clearly the presence of $1384 cm^{-1}$ absorption. As there are much more NO_3^- ions in the solution during re-oxidation than TsO^- ions de-intercalated from reduction of the starting film, the counter anions re-intercalated into the film during re-oxidation must naturally NO_3^- instead of TsO^-. These facts demonstrate without any ambiguity that the processes involved in the electrochemical oxidation ("doping") and reduction ("de-doping") are actually charge transfer intercalation and de-
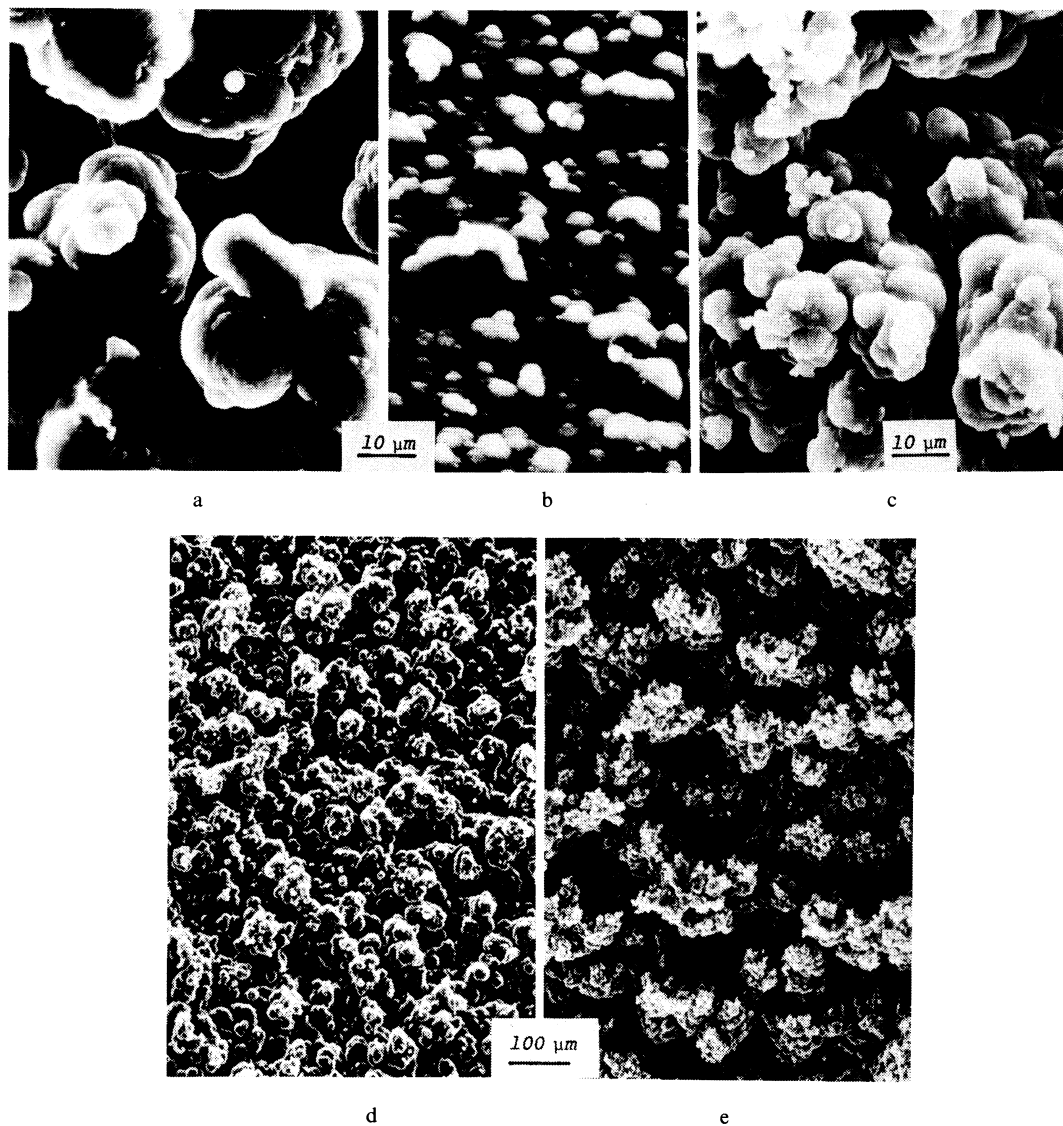

Figure 14. SEM photographs of (a) a TsO^- intercalated PPy film; (b) the film after electrochemical reduction; (c) the film after electrochemical re-oxidation; (d) and (e) the same as (a) and (c) respectively at lower magnification.

intercalation of the counter ions in the PPy film.[8] By intercalation here it does not necessary mean the incorporation of the counter ions between lattice planes, as PPy is in fact amorphous, but between chains in the macromolecular condensed state. Kaufman *et al.*[18] deduced from their electrochemical voltage spectroscopy that during electrochemical reduction of a ClO_4^- intercalated PPy film in a THF solution of $LiClO_4$ the process involved is not the de-intercalation of ClO_4^- anion but the intercalation of Li^+ cation leading to a compensation of charges. This statement is very probably not true. We electrochemically reduced a ClO_4^- intercalated PPy film in an aqueous solution of $LiClO_4$, the IR spectra of the film before and after reduction show clearly the presence and absence respectively of the absorption bands at $627 \, cm^{-1}$ and at $1120, 1145 \, cm^{-1}$ characteristic of the ClO_4^- ion as shown in Figure 13. Only in the case of a polymeric counter anion like polyvinyl sulfate intercalated PPy film it has been found by Iyoda *et al.*[5] that during electrochemical reduction in a solution of K salt of polyvinyl sulfate the polymeric counter anions are not de-intercalated but K^+ cations go into the film instead.

Treatment of a conducting PPy film with NaOH or NH_4OH solution leads to an enormous drop of its conductivity, from $10^2 \, S \, cm^{-1}$ dropping to $10^{-4} \, S \, cm^{-1}$. This has been termed chemical compensation. The IR spectrum of a NO_3^- intercalated PPy film after being immersed in 2 M NaOH solution for 6 h shows the absence of the NO_3^- counter anion as shown also in Figure 12. Judging from the conductivity value being still two orders of magnitude higher than that of an electrochemically reduced film and the broadness of the absorption bands resembling an intercalated film we suppose that there may be residual charged defects in the PPy chain due to incompleteness of de-intercalation or very probably due to OH^- intercalation.

SEM observation of a TsO^- intercalated PPy film and the film after electrochemical reduction and re-oxidation reveals profound morphological changes occurring in these processes as shown in Figure 14. This indicates a
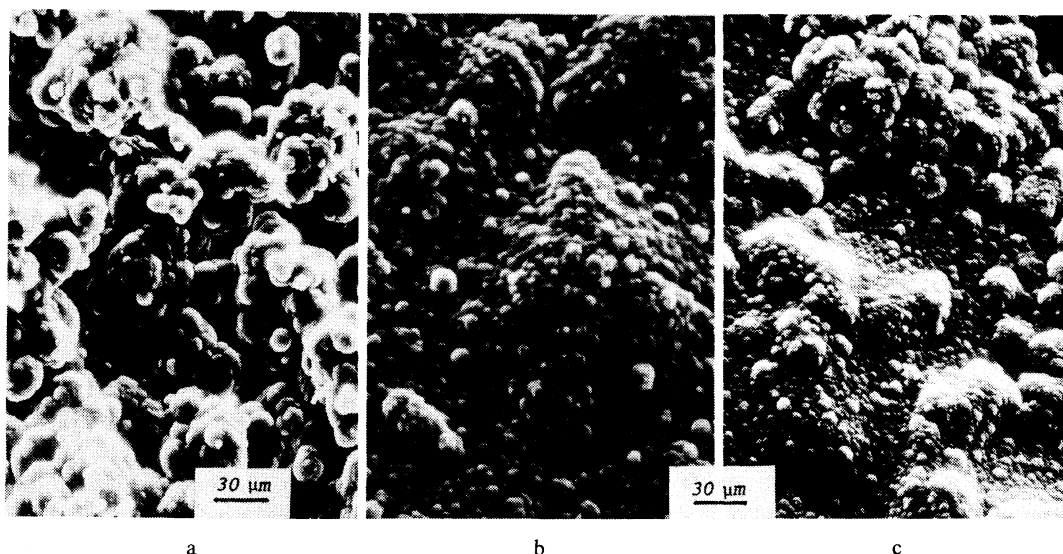

a   b   c

Figure 15. SEM photographs of (a) a NO_3^- intercalated PPy film; (b) the film after electrochemical reduction; (c) the film after electrochemical re-oxidation.

disruption and re-organization of the macro-molecular aggregation in the solid state during these processes.[8] Similar results are obtained for NO_3^- intercalated PPy as shown in Figure 15. These results seem to support the view of chemical structural change during reduction and re-oxidation discussed in the previous section, as analogous observations on inter-calated polythiophene film show no signifi-cant changes in morphology during electro-chemical reduction and re-oxidation.[22]

MOLECULAR COMPOSITE

Fiber reinforced plastics have been widely used as strong and light weight materials as metal substitutes. The idea of improving mechanical properties of a flexible chain polymer by dispersing in it a fibre of large aspect ratio has led to the development of "molecular composite" by Takayanagi[23] and by Helminiak[24] using methods of co-precipita-tion and block co-polymerization to disperse a rigid rod-like macromolecule of large intrin-sic aspect ratio in a matrix of flexible chain polymer. Although the dispersion achieved has so far not been able to reach truly mo-lecular level, very attractive results have been obtained in getting a light weight, high modulus, high strength and heat resistant ma-terial comparable in mechanical properties of aluminum.[25] Conducting polymers are conjugated chain macromolecules which are expected to behave as rigid rods. Graft-block copolymers of polyacetylene onto polyiso-prene[26] and polybutadiene[27] are soluble conducting polymers and belong to the cate-gory of molecular composite. A more pro-mising way of preparing a molecular com-posite of conducting polymers is to polym-erize in situ acetylene, pyrrole, thiophene etc. in a flexible polymer matrix. Wnek[28] impregnated LDPE film with a catalyst so-lution to polymerize acetylene gas in the film and a flexible film of conductivity $10 \, \mathrm{S \, cm^{-1}}$ resulted. For a PPy molecular composite

the in situ polymerization of pyrrole in a flex-ible polymer film can be carried out either electrochemically or chemically. Electro-chemical growth of intercalated PPy in lightly crosslinked polyvinyl alcohol[29] and poly-vinyl chloride[30] films on Pt electrode from aqueous and acetonitrile solution respectively has been successfully conducted to give com-posite polymer films of conductivities of 10^{-1} to $10 \, \mathrm{S \, cm^{-1}}$. Chemical polymerization of pyr-role by persulfate, ceric sulfate and Lewis acids like $FeCl_3$, $MoCl_5$, and $RuCl_3$ can be utilized for the preparation of molecular composites of PPy with commonly available flexible poly-mers. The flexible polymer film is swollen with solvent containing the polymerization catalyst and then the film is exposed to pyrrole vapor resulting in the in situ polymeriza-tion.[31-33] In the other way the flexible poly-mer film can be swollen with a solvent con-taining pyrrole and then the film is brought in contact with the polymerization catalyst solution to carry out the in situ polymeriza-tion of pyrrole in the film.[34] Chemically polymerized and intercalated PPy powder can be mechanically incorporated into plastics to give molded composites[35] but probably not in the proper sense of a molec-ular composite. Or, polymeric electrolytes like polystyrene sulfonate or polyvinyl sul-fate[5] and sulfonated SBS triblock with the B block hydrogenated,[6] used as the supporting electrolyte during electrochemical polymeri-zation of pyrrole can also lead to molecular composites of PPy. All these molecular com-posites of PPy can have a conductivity ranging from 10^{-3} to $10 \, \mathrm{S \, cm^{-1}}$.

In our laboratory we have been able to prepare molecular composites of PPy with a wide variety of commercial plastics like Nylon, PVC, PVA, PVAc, polyvinyl butyral, amor-phous PET, cellophane, viscose, cellulose, cot-ton, wool, natural rubber, Nafion film etc. through in situ polymerization of pyrrole im-bibed in the polymer film or fiber with a proper solvent.[36] The bulk conductivity (not the sur-
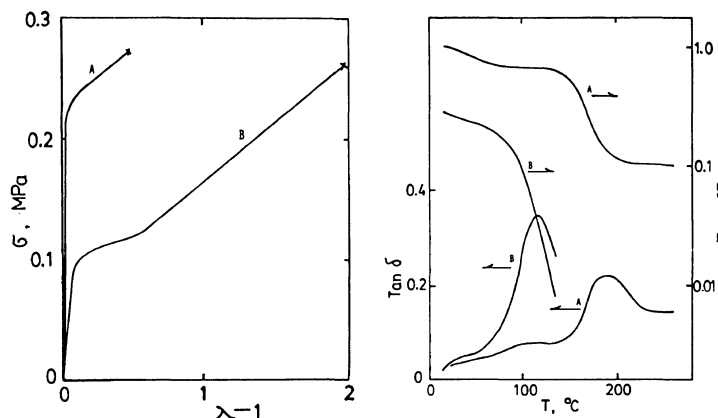
Figure 16. Stress strain behavior under stretching at 80% per min (left) and dynamic mechanical properties (right) of PPy/Nafion composite (A) as compared to Nafion film (B).

face conductivity) can be controlled by the polymerization condition to vary from 10^{-9} to $10^{-2}\,\mathrm{Scm^{-1}}$. The low conductivity of a PPy/Nafion composite has been shown to have an island and sea morphology with PPy domains of 80 nm diameter.[34] These PPy molecular composites are potential materials for anti-static applications. PPy composites with conductivities higher than $10\,\mathrm{Scm^{-1}}$ may find applications in EMI shielding. The incorporation of rigid chain PPy into a flexible polymer does actually show a several fold increase of modulus with decrease of the extension at break as examplified in Figure 16,[34] and render the plastics hydrophobic.

Molecular composites of conducting polymers are new class of materials with wide range of potential applications. A rapid development in this area is to be expected.

REFERENCES

1. A. Dall'Olio, G. Dascola, V. Varacca, and V. Bocche, *Compt. rend. l'Acad. Sci. (Paris)*, **C267**, 433 (1968).
2. A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 635 (1979).
3. W. Wernet, M. Monkenbusch, and G. Wegner, *Mol. Cryst. Liq. Cryst.*, **118**, 193 (1985).
4. M. Satoh, K. Kaneto, and K. Yoshino, *Jpn. J. Appl. Phys.*, **24**, L423 (1985).
5. T. Iyoda, A. Ohtani, T. Shimidzu, and K. Honda, *Chem. Lett.*, 687 (1986).
6. N. Bates, M. Cross, R. Lines, and D. Walton, *J. Chem. Soc., Chem. Commun.*, 871 (1985).
7. X. Bi, Y. Yao, M. Wan, P. Wang, K. Xiao, Q. Yang, and R. Qian, *Makromol. Chem.*, **186**, 1101 (1985).
8. R. Qian, J. Qiu, and D. Shen, Abstr. ICSM 86, p 308; *Synth. Met.*, in press.
9. J. Qiu, M. S. thesis, Institute of Chemistry, Academia Sinica, 1986.
10. R. Qian, J. Qiu, and B. Yan, *Synth. Met.*, **14**, 81 (1986).
11. S. Asavapiriyanont, G. K. Chandler, G. A. Gunawardena, and D. Pletcher, *J. Chem. Soc., Chem. Commun.*, 871 (1985).
12. N. F. Mott and E. A. Davis, "Electronic Processes in Non-Crystalline Materials," 2nd ed, Clarendon Press, Oxford, 1979, p 34.
13. Y. Shen, K. Carneiro, C. Jacobsen, R. Qian, and J. Qiu, Abstr. ICSM 86, p 209; *Synth. Met.*, in press.
14. L. B. Coleman, *Rev. Sci. Instru.*, **49**, 58 (1978).
15. M. Wan, D. Zhu, M. Li, and R. Qian, *Kexue Tongbao*, **28**, 1623 (1983).
16. M. Wan, P. Wang, Y. Cao, F. Wang, X. Zhao, and Z. Gong, *Solid State Commun.*, **47**, 759 (1983).
17. P. Wang, M. Wan, X. Bi, Y. Yao, and R. Qian, *Acta Phys. Sin.*, **33**, 1771 (1984).
18. J. H. Kaufman, K. K. Kanazawa, and G. B. Street, *Phys. Rev. Lett.*, **53**, 2461 (1984).
19. R. Jones and G. P. Beau, "The Chemistry of Pyrroles," Academic Press, New York, N. Y., 1977, p 117.

20. G. B. Street, T. C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott, and G. Weiser, *Mol. Cryst. Liq. Cryst.*, **83**, 253 (1982).

21. L. Oddi, R. Capelletti, R. Fiescher, M. P. Fontana, G. Ruani, V. Bocchi, and G. P. Gardini, *Mol. Cryst. Liq. Cryst.*, **118**, 179 (1985).

22. Y. Cao and H. Zhang, private communication.

23. M. Takayanagi, Japan Patent appl. S52-131436 (1977); U. S. Patent appl. 958324 (1978); *Pure Appl. Chem.*, **55**, 819 (1983).

24. T. E. Helminiak, U. S. Patent appl. 902525 (1978).

25. W. W. Adams, T. E. Helminiak, and A. Visvanathan, Proceedings, IUPAC MACRO 82, 1982, p 828.

26. F. S. Bates and G. I. Baker, *Maceomolecules*, **16**, 704 (1983).

27. S. Destri, M. Calellani, and A. Bolognesi, *Makromol. Chem., Rapid Commun.*, **5**, 353 (1984).

28. G. E. Wnek, Proceedings, IUPAC MACRO 82, 1982, p 409; U. S. Patent appl. 4394304 (1982).

29. S. E. Lindsey and G. B. Street, *Synth. Met.*, **10**, 67 (1984).

30. O. Niwa and T. Tamamura, *J. Chem. Soc., Chem. Commun.*, 817 (1984).

31. A. Pron, B. Raynor, P. Bernier, S. Lefrant, W. Fabianowski, and C. Budrowski, Abstr. ICSM 86, 1986, p 177.

32. R. Sugimoto, H. B. Gu, S. Hayashi, and K. Yoshino, Abstr. ICSM 86, 1986, p 192.

33. S. Miyata, T. Ojio, and Y. E. Wang, Abstr. ICSM 86, 1986, p 427.

34. R. Qian and Y. Chen, Proceedings, Plastics Conference, The Plastics & Rubber Institute, Singapore, 1986.

35. G. P. Gardini and V. Bocchi, Abstr. ICSM 86, 1986, p 194.

36. Institute of Chemistry, Academia Sinica, Chinese Patent appl. 86101389 (1986).