Synthesis and Characterization of Some Polyaniline–Organic Acceptor Complexes

S. H. KHOR, K. G. NEOH, and E. T. KANG,* *Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 0511*

Synopsis

The charge transfer (CT) interactions between polyemeraldine (PEM) and six organic electron acceptors were studied. The complexing ability of the acceptors, based on the maximum attainable electrical conductivity of the resulting complex, could be arranged in the following ascending order: tetrachloro-*p*-benzoquinone (*p*-chloranil), tetrafluoro-*p*-benzoquinone (*p*-fluoranil), tetrabromo-*o*-benzoquinone (*o*-bromanil), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), tetrachloro-*o*-benzoquinone (*o*-chloranil), and tetracyanoethylene (TCNE). Conductivity in the order of 10^{-1} S/cm was achieved in the PEM/TCNE complex. The complexes were also characterized by infrared (IR) absorption spectroscopy, thermogravimetric (TG) analysis, and X-ray photoelectron spectroscopy (XPS). In most complexes, the CT interactions have proceeded further than the formation of pure molecular complexes. However, the mechanism of CT interaction was found to be analogous to that of protonation of PEM by protonic acids.

INTRODUCTION

In recent years, a great amount of renewed work[1-4] has been done on the century-old[5] aniline family of polymers. This is partly because of the interesting ways in which the oxidation states of polyaniline can be varied from the fully oxidized "pernigraniline," through the 50% oxidized "emeraldine" to the fully reduced "leucoemeraldine.[2]" In addition, the electrical conductivity of the polymer could be increased from about 10^{-11} S/cm to over 1 S/cm by protonation with protonic acids, such as HCl[1,2] or by electrochemical doping.[4,6] The former differs from the "doping" process of other conjugated polymers in that protonation does not involve a change in the number of electrons associated with the polymer backbone.

Most of the recent work on polyaniline has been centered on the protonation of polyemeraldine (PEM) with HCl. In the past, organic electron acceptors such as the various benzoquinones have been used to enhance the conductivity of electroactive polymers like polypyrrole,[7] polyphenylacetylene,[8] and polyvinylpyridines.[9] Accordingly, it should be interesting to examine how these organic electron acceptors influence the electrical properties of polyaniline. The organic electron acceptors used in this work include tetrachloro-*o*-benzoquinone (*o*-chloranil), tetrachloro-*p*-benzoquinone (*p*-chloranil), tetrabromo-*o*-benzoquinone (*o*-bromanil), tetrafluoro-*p*-benzoquinone (*p*-fluoranil), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and tetracyanoethylene (TCNE). When-

---

* To whom correspondence should be addressed.

ever possible, comparisons will be made between the organic acceptor "doping" and the protonic acid "doping."

EXPERIMENTAL

Polymer Samples

Polyemeraldine hydrochloride was prepared at 0–5°C by the oxidative polymerization of aniline in 1 M aqueous HCl by ammonium persulfate.[2,3] It was converted to the emeraldine base by treatment with excess 0.5 M aqueous NH_4OH and dried by pumping under reduced pressure. Complex formation with the organic acceptors was carried out by dispersing the finely ground PEM in the acetonitrile solution of the acceptor containing various amounts of the acceptor. Each reaction mixture was vigorously agitated under a nitrogen atmosphere. The solvent was then allowed to evaporate at room temperature. The final drying of the sample was achieved by pumping under reduced pressure. The organic acceptors used consisted of o-chloranil, p-chloranil, o-bromanil, p-fluoranil, DDQ, and TCNE, obtained from Aldrich Chemical Co. All acceptors were recrystallized from appropriate organic solvents before use.

Polymer Characterization

Electrical conductivities of the PEM/organic acceptor complexes were measured using both the standard collinear four-probe and two-probe techniques on compressed pellets. Conductivities below room temperature were measured *in situ* in a liquid nitrogen cryostat and in the presence of an inert atmosphere. The infrared (IR) absorption spectra were measured on a Perkin-Elmer Model 682 spectrophotometer with the polymer samples dispersed in KBr. Thermogravimetric analyses (TGA) were carried out using a Netzsch Model STA 409 simultaneous TG-DTA apparatus, at a heating rate of 10°C min^{-1} in nitrogen. X-ray photoelectron spectroscopy (XPS) measurements were performed for the various PEM/organic acceptor complexes. Sample measurements were made on a VG ESCALAB MkII spectrometer with a MgKα X-ray source (1253.6 eV photons). The X-ray power supply was run at 12 kV and 10 mA. All core-level spectra were referenced to the Cls neutral carbon peak at 284.6 eV. In spectral deconvolution, the peak width (f.w.h.m.) was maintained constant for all components in a particular spectrum.

RESULTS AND DISCUSSION

Electrical Properties

The electrical conductivity of the polyemeraldine (PEM)/organic acceptor complexes is strongly dependent on the type and amount of the acceptor incorporated into the complexes. Figure 1 shows how the conductivity of the six complexes varies with the acceptor/monomer mole ratio. For each complex, there appears to be an optimum amount of acceptor incorporated to achieve maximum conductivity. With TCNE, DDQ, o-chloranil and p-fluoranil, the
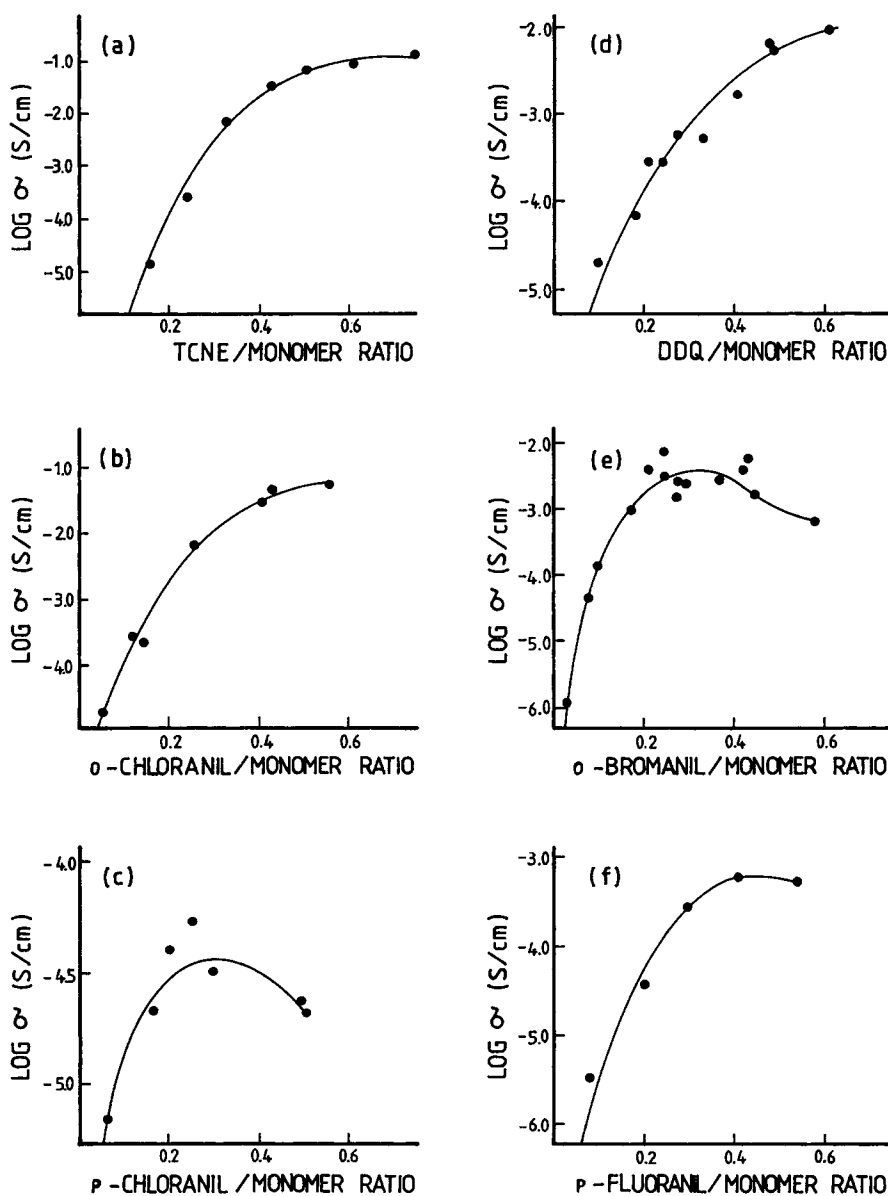
Fig. 1.   Electrical conductivity (σ) of polyemeraldine/organic acceptor complexes as a function of acceptor concentration.

maximum conductivity occurs close to an acceptor/monomer mole ratio of 0.5. For o-bromanil and p-chloranil the corresponding ratio for maximum conductivity is about 0.3. The decline in conductivity as the acceptor concentration increases beyond the optimum may be due to the presence of unreacted or loosely complexed acceptor molecules.

At optimum acceptor/monomer ratio, the highest conductivity measured is of the order of 10^{-1} S/cm, and this is achieved in the PEM/TCNE complex.

The maximum conductivity of the complexes decreases in the order PEM/ TCNE > PEM/o-chloranil > PEM/DDQ, PEM/o-bromanil > PEM/p-fluoranil > PEM/p-chloranil. The electrical conductivity can be expected to be affected by the nature and extent of the charge transfer interaction between the acceptor and the polymer. Comparison of the conductivity data from the four halobenzoquinones (o- and p-chloranil, o-bromanil, and p-fluoranil) suggests that the "ortho structure" presents less steric hindrance to the charge transfer interaction.

The variation of electrical conductivity (σ) with temperature (T) for the PEM/TCNE complex of high conductivity was measured at and below room temperature. An apparent linear fit of the experimental data is obtained when ln σ is plotted vs. $T^{-1/4}$ for the temperatures between 120 and 300 K in four-probe conductivity measurements [Fig. 2(a)]. The $\frac{1}{4}$ power temperature dependence has also been observed in the protonated PEM,[10,11] as well as in other polymers with conjugated backbone, such as polyacetylene[12] and the electrochemically[13] and chemically[14] synthesized polypyrrole complexes. This behavior has been interpreted in terms of Mott's model[15] of variable range hopping between localized states near the Fermi surface. The physical significance of the $\frac{1}{4}$ power temperature dependence, however, should be interpreted with care in view of the fact that $\frac{1}{2}$ power temperature dependence[16] has also been reported for the emeraldine salt polymer. Furthermore, the inadequacy of the ordinary four probe conductivity measurements in overcoming the interfibrillar, intergranular, and intercrystallitic contact resistance of polymer samples with metal-like conductivity has also been reported and partially resolved using the voltage shorted compaction technique.[12] The activation energy E_a of the present TCNE complex can be obtained from the ln σ vs. $1/T$ plot, as shown in Figure 2(b). An E_a value of about 0.07 eV is observed. This value is comparable to that of 0.05 eV reported for some of the polyemeraldine salts.[11]

Thermogravimetric Analysis

The thermogravimetric (TG) scans of the PEM/organic acceptor complexes generally show a small initial weight loss ($\sim$ 5%) followed by a plateau and
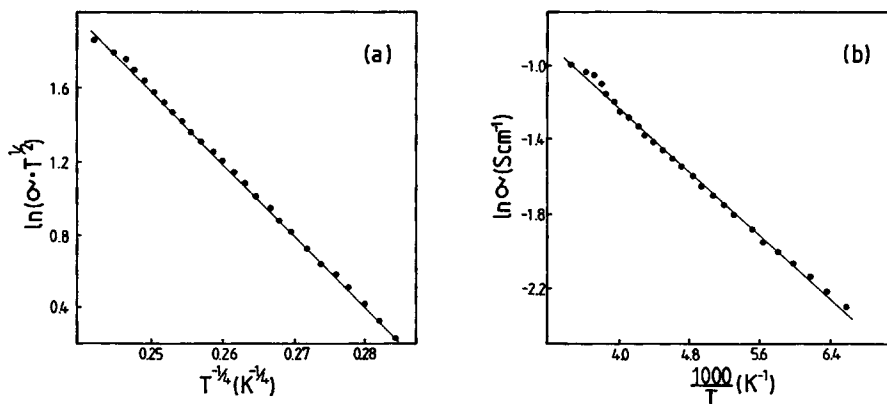

Fig. 2.   Temperature dependence of the electrical conductivity of the polyemeraldine/TCNE complex in four-probe conductivity measurements.

then another weight loss step. This is illustrated by the TG scans of the PEM/ TCNE and PEM/DDQ complexes in Figure 3. These two complexes have an acceptor/monomer ratio of about 0.5 and at this ratio, the conductivity is maximum. For comparison purposes, the TG scans of emeraldine hydrochloride and emeraldine base are also plotted in Figure 3. The initial weight loss which occurs below 100°C is probably due to residual solvent (and/or HCl in the case of emeraldine hydrochloride) from the synthesis and doping processes. The emeraldine base exhibits the highest thermal stability with minimal weight loss below 500°C, and even at 700°C it retains 75% of its original weight. In contrast, the emeraldine hydrochloride sample decomposes at around 225°C. The TG scans of the PEM/organic acceptor complexes at acceptor/monomer ratios which resulted in maximum conductivity indicate that the PEM/o-bromanil, PEM/DDQ, and PEM/TCNE complexes decompose at temperatures almost identical to that of emeraldine hydrochloride, while the remaining three complexes decompose at lower temperatures. With the exception of the PEM/p-chloranil complex, the decomposition temperatures of these complexes are higher than those of the respective organic acceptors and hence this indicates that there is insignificant amount of unreacted acceptor in the complexes at the acceptor/monomer ratios which result in maximum conductivity.

Infrared Absorption Spectroscopy

Some gradual changes in the IR absorption spectra of PEM are observed upon progressive "doping" with the organic acceptors. In PEM base, absorption
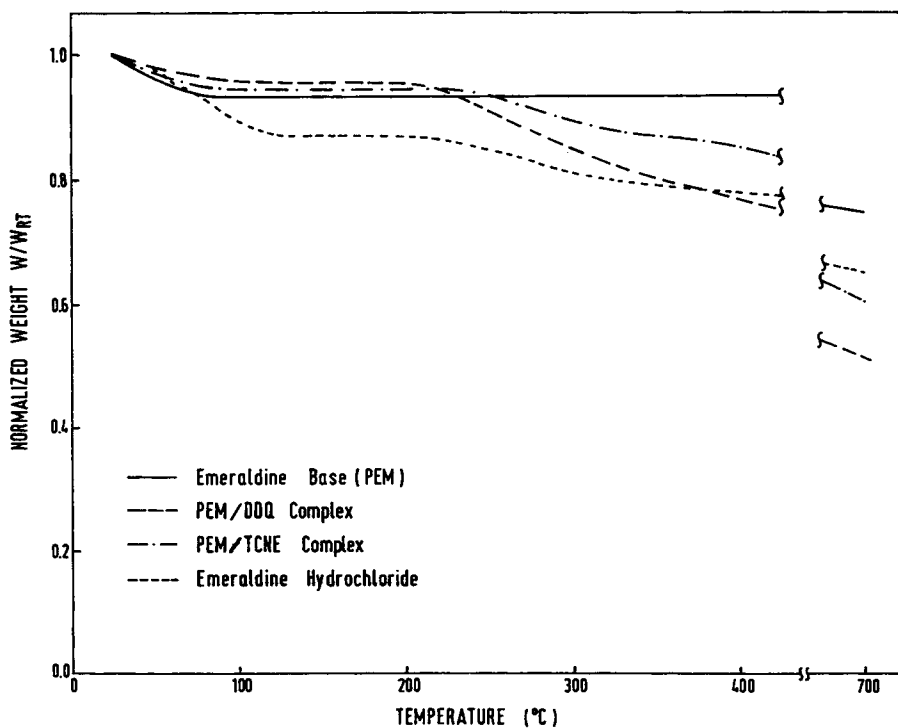

Fig. 3.   TG scans of polyemeraldine hydrochloride, polyemeraldine base, and some of the polyemeraldine/organic acceptor complexes in N_2.

bands at 1590 and 1502 cm^{-1} have been associated with the aromatic ring stretching modes.[17,18] The peaks are broadened and shifted somewhat towards the longer wavelength upon gradual incorporation of the organic acceptors. For example, the absorption frequencies of these two peaks gradually shift, respectively, from 1590 to 1570 cm^{-1} and from 1500 to 1492 cm^{-1} upon increasing the o-chloranil/monomer ratio from 0.02 to 0.25 [Figs. 4(a) and (b)]. Similar red shifts have also been observed in the IR spectrum of PEM upon acid protonation and have been associated with the conversion of quinoid rings to benzenoid rings.[18] Thus, similar changes in the IR absorption spectra of PEM are observed upon charge transfer interaction with the organic acceptors and upon protonation. These readily suggest that the structural changes associated with the two "doping" processes must closely resemble one another.

Furthermore, the absorption band at 1145 cm^{-1}, which has been associated with electrical conductivity in polyaniline,[17,19] strengthened and broadened gradually upon progressive incorporation of the organic acceptors. It is also red shifted to about 1130 cm^{-1} at high dopant concentration [Fig. 4(b)]. These observations are consistent with an increase in the degree of delocalization of electrons on the polymer and the corresponding increase in the conductivity of the sample as the acceptor level increases.

An interesting feature of the IR absorption spectrum of the PEM–TCNE complex is the position of the C≡N stretching mode in the region of 2100–2300 cm^{-1} [Fig. 4(c)]. By comparing the C≡N stretching of molecular TCNE with that of the PEM/TCNE complex, the absorption doublet at 2240 and 2230 cm^{-1} has shifted to below 2200 cm^{-1} in the latter. Similar peak features but of reduced intensity could also be observed in complexes involving DDQ as an acceptor. Thus, the IR results are consistent with the formation of the cyano radical anions[20] in both PEM/TCNE and PEM/DDQ complexes.

With the exception of the absorption due to the C≡N group, the absorption bands due to the organic acceptors are not clearly visible in most of the complexes. The absence of anionic absorption bands has also been reported in other conjugated polymer complexes involving inorganic[21] and organic acceptors.[7] In fact, for organic complexes, the degree of changes in the IR absorption spectrum on complex formation, compared with the sum of the spectrum of the two components, has been used to distinguish between weak charge transfer complexes and the products of electron-transfer reaction.[22]

XPS Measurements

The N1s XPS core-level spectrum of all the present PEM/organic acceptor complexes shows the presence of a high binding energy (BE) tail at energies above 401 eV, in addition to the main component peak at about 399.3 eV. Similar line-shape and BE have also been observed in the protonated PEM and the high BE tail has been attributed to the formation of positively charged nitrogen.[23,24] The halogen core-level spectra for all the complexes involving the halobenzoquinone, such as o-chloranil, p-chloranil, o-bromanil, p-fluoranil, and DDQ, can be fitted with peak components at BE positions corresponding to those for covalent and ionic halogen species. As an example, Figures 5(a)–(c) show the respective N1s, Br3d, and O1s core-level spectra for a PEM/o-bromanil complex at an acceptor/monomer ratio of 0.27. The presence of halogen
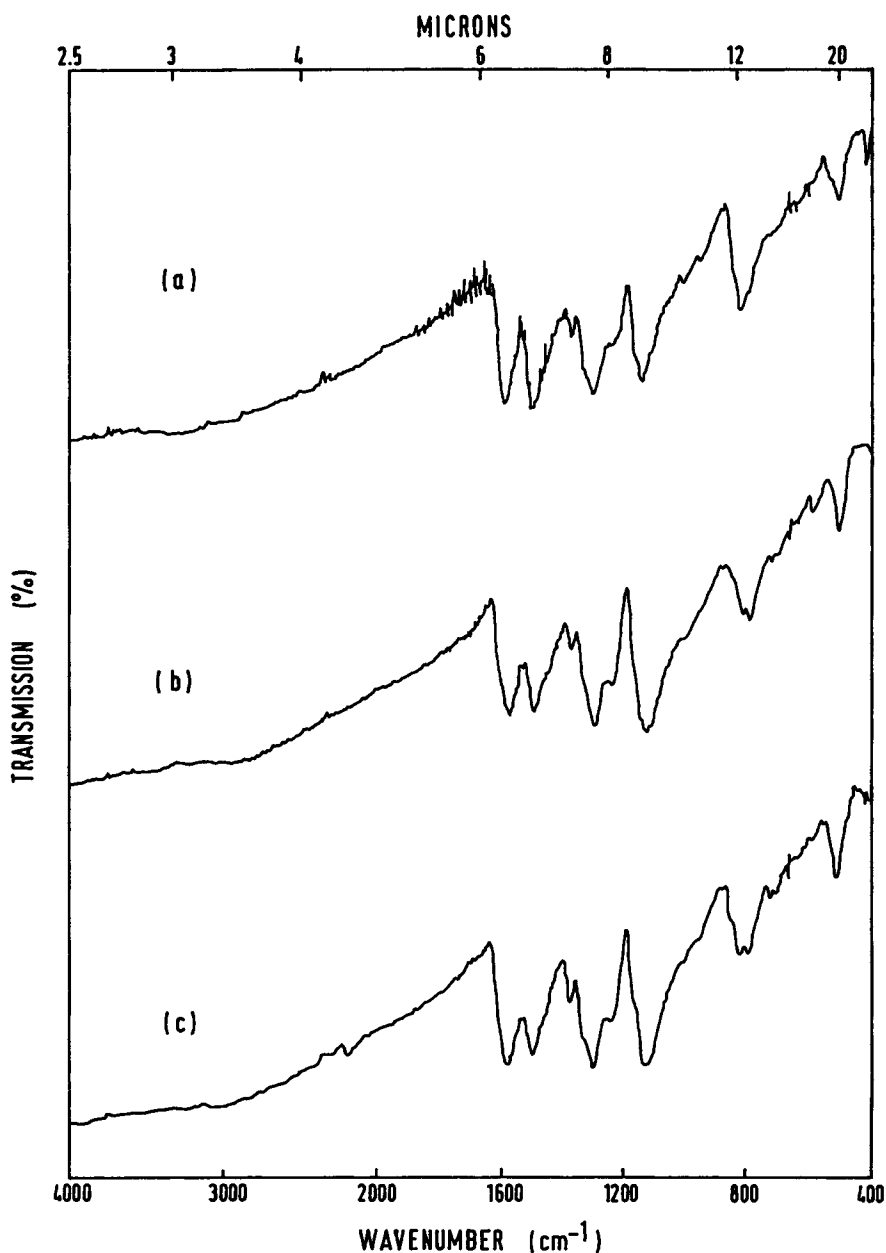
Fig. 4. IR absorption spectra: (a) and (b) the polyemeraldine/o-chloranil complexes at acceptor/monomer ratios of 0.02 and 0.25, respectively, and (c) the polyemeraldine/TCNE complex at acceptor/monomer ratio of 0.51.

anions in the present PEM/halobenzoquinone complexes suggests that the charge transfer interactions must have proceeded further than the formation of pure molecular complexes. Thus, some of the halogen atoms of the halobenzoquinone acceptor may have been replaced by the formation of linkage between the polymer and the acceptor. Furthermore, the O1s XPS core-level spectra
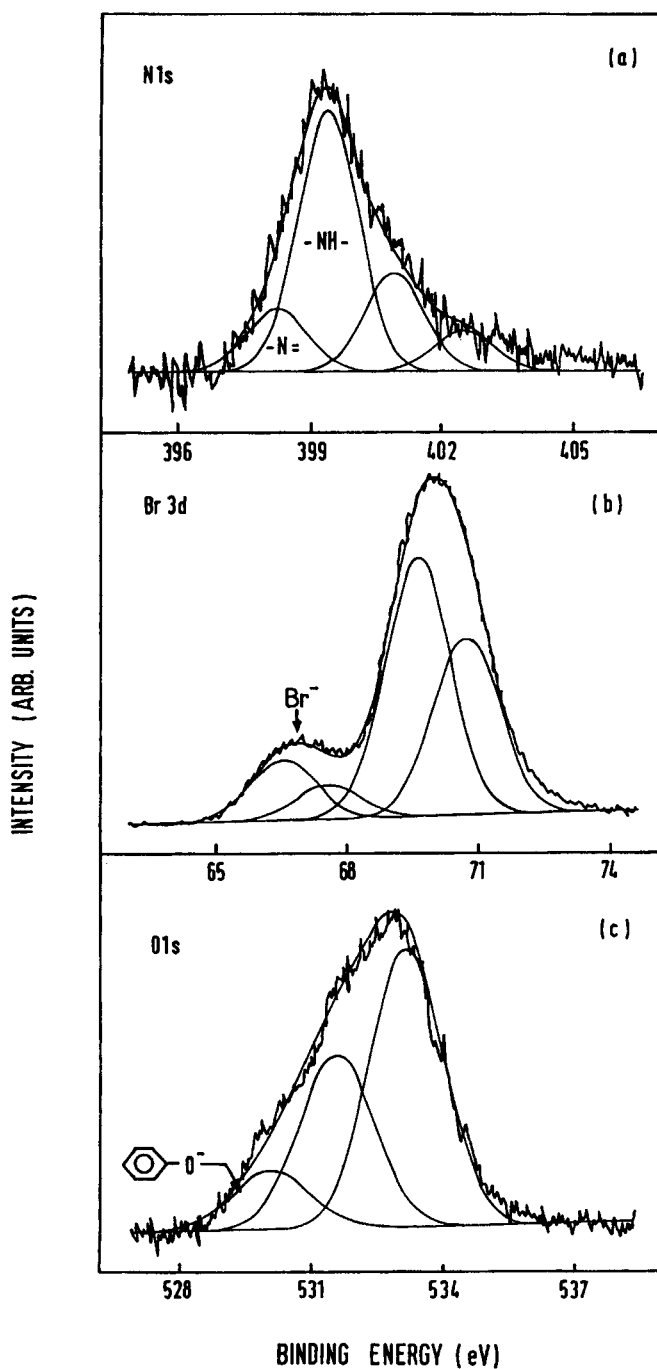
Fig. 5.   (a) N1s, (b) Br3d, and (c) O1s XPS core-level spectra of a polyemeraldine/*o*-bromanil complex at an acceptor/monomer ratio of 0.27.

for all of the complexes reveal the presence of three environments for oxygen. The peak component, which is shifted by about -1.5 eV from the neutral carbonyl peak at about 531.5 eV, is attributable to the formation of benzoquinone or semi-benzoquinone anion.[25,26] On the other hand, however, a $+1.5$ eV shift in BE strongly suggests that some of the carbonyl oxygen are involved in the formation of $C-O-$ structure, such as the formation of linkage between carbonyl oxygen and positively charged nitrogen of the polymer.[25] Furthermore, surface oxidation products and contaminants may also have contributed to some extent to the present O1s spectrum, as in the case of electrochemically prepared polyaniline complexes.[27] In all of the present halobenzoquinone complexes, the proportion of the oxygen anion does not appear to vary substantially from sample to sample. However, the ease of the formation of halogen anion shows a strong dependence on the type of acceptor. It decreases in the order of o-chloranil > DDQ > o-bromanil > p-fluoranil, p-chloranil, as in the case of electrical conductivity. Thus, the formation of halogen anions is facilitated by the ortho structure, probably as a result of substantially less steric hinderance encountered at the C_4 position.

Finally, the CT interaction involving the cyano group of DDQ and TCNE cannot be easily resolved from the XPS results. The N1s envelope of the polymer which consists of the imine, amine,[28] and positively charged nitrogen overlaps with that of the neutral cyano group and the cyano radical anions of the TCNE acceptor. Thus, although the presence of cyano anions has been suggested by the IR absorption spectra and is required to account for the formation of positively charged nitrogen in the PEM/TCNE complexes, the proportion of the cyano anion cannot be quantitatively and unambiguously determined.

Upon treatment of the present PEM/organic acceptor complexes with 1.0 M NH_4OH solution, the polymer returned to the violet-blue color characteristic of PEM. This is accompanied by a complete loss of the electrical conductivity of the sample. This agrees with the UV-visible absorption spectra of the resulting NH_4OH solutions which show that a substantial amount of the acceptor molecules has been stripped off the polymer complexes. However, in the case of PEM/TCNE and PEM/DDQ complexes, the IR absorption peaks due to the cyano groups at around 2200 cm^{-1} persisted even after rigorous treatment of the complex with 5 M NH_4OH solution for more than 20 h.

Based on the present experimental evidence, the possible mechanisms involved in the charge transfer between PEM and the halobenzoquinones are shown in Figure 6. Similar complex structures have been suggested for the CT interactions between p-chloranil and the nitrogen atom of molecular pyridine ($=N-$ structure) to account for the presence of positively charged pyridinium nitrogen and the chloride and benzoquinone anion.[25] Careful examination of the structure proposed in Figure 6(a) suggests that the charge transfer interaction between PEM and the halobenzoquinones is analogous to that of protonation by HCl, with the hydrogen atoms in the latter replaced by the partially dehalogenated halobenzoquinone rings. The structure of the PEM/TCNE complexes cannot be resolved without further experimental evidence. The presence of the cyano groups and their persistence even after vigorous treatment with a base would probably suggest a covalently bonded TCNE anion structure similar to that postulated during the charge transfer complex formation between TCNE and N-methylaniline or N,N-dimethylaniline.[29]
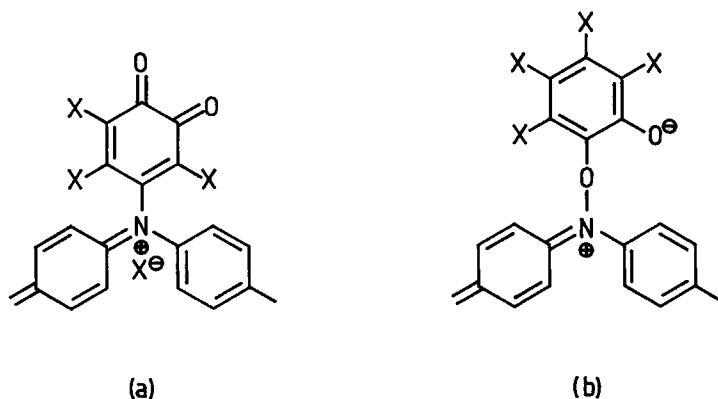
Fig. 6.   Possible mechanisms of charge transfer interaction involving polyemeraldine and the halobenzoquinones.

CONCLUSION

Charge transfer complexes involving polyemeraldine and *o*-chloranil, *p*-chloranil, *o*-bromanil, *p*-fluoranil, DDQ, and TCNE have been successfully prepared. In all cases, the electrical conductivity showed a strong dependence on the acceptor concentration at low acceptor loadings. Conductivity as high as 10^{-1} S/cm was observed in the TCNE complexes. The physicochemical properties of the complexes were studied by low temperature conductivity measurements, IR absorption spectroscopy, TG analysis, and XPS. The CT interaction between PEM and most of the organic acceptors was found to resemble the process of protonation in certain aspects.

References

1. J. C. Chiang and A. G. MacDiarmid, *Synth. Metals,* **13,** 193 (1986).

2. A. G. MacDiarmid, J. C. Chiang, A. F. Richter, and A. J. Epstein, *Synth. Metals,* **18,** 285 (1987).

3. S. P. Armes and J. F. Miller, *Synth. Metals,* **22,** 385 (1988).

4. A. F. Diaz and J. A. Logan, *J. Electroanal. Chem. Interfacial Electrochem.,* **111,** 111 (1980).

5. A. G. Green and A. E. Woodhead, *J. Chem. Soc.,* 2388 (1910).

6. A. G. MacDiarmid, L. S. Yang, W. S. Huang, and B. D. Humphrey, *Synth. Metals,* **18,** 393 (1987).

7. E. T. Kang, K. G. Neoh, T. C. Tan, and Y. K. Ong, *J. Polym. Sci. Polym. Chem. Ed.,* **25,** 2143 (1987).

8. Y. Kuwane, T. Masuda, and T. Higashimura, *Polym. J.,* **12,** 387 (1980).

9. E. T. Kang and Y. K. Ong, *Solid State Commun.,* **57,** 587 (1986).

10. J. P. Travers, J. Chroboczek, F. Genoud, M. Nechtchein, A. Syed, E. M. Genies, and C. Tsintaris, *Mol. Cryst. Liq. Cryst.,* **121,** 195 (1985).

11. W. R. Salaneck, B. Liedberg, O. Inganas, R. Erlandson, L. Lundstrom, A. G. MacDiarmid, M. Halpern, and N. L. D. Somasiri, *Mol. Cryst. Liq. Cryst.,* **121,** 191 (1985).

12. M. Wan, P. Wang, Y. Cao, R. Quian, F. Wang, X. Zhao, and Z. Gong, *Solid State Commun.,* **47,** 759 (1983).

13. A. Watanabe, M. Tanaka, and J. Tanaka, *Bull. Chem. Soc. Jpn.,* **54,** 2278 (1981).

14. E. T. Kang, K. G. Neoh and H. C. Ti, *Solid State Commun.,* **60,** 457 (1986).

15. N. F. Mott and E. A. Davis, *Electronic Process in Non-Crystalline Materials,* 2nd ed., Clarendon, Oxford, 1979, p. 34.

16. F. Zuo, M. Angelpoulos, A. G. MacDiarmid, and A. J. Epstein, *Phys. Rev. B,* **36,** 3475 (1987).

17. J. Tang, X. Jing, B. Wang, and F. Wang, *Synth. Metals,* **24,** 231 (1988).

18. Y. H. Kim, C. Foster, J. Chiang, and A. J. Heeger, *Synth. Metals,* **25,** 49 (1988).

19. Y. Cao, S. Li, Z. Xue, and D. Guo, *Synth. Metals,* **16,** 305 (1986).

20. J. Stanley, D. Smith, B. Latimer, and J. P. Devlin, *J. Phys. Chem.,* **70,** 2011 (1966).

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

22. R. Foster, *Organic Charge-Transfer Complexes,* Academic, London, 1969, Chap. 4.

23. W. R. Salaneck, I. Lundstrom, T. Hjertberg, C. B. Duke, E. Conwell, A. Paton, A. G. MacDiarmid, N. L. D. Somasiri, W. S. Huang, and A. F. Richter, *Synth. Metals,* **18,** 291 (1987).

24. H. S. Munro, D. Parker, and J. G. Eaves, *Springer Ser. Solid-State Sci.,* **76,** 257 (1987).

25. K. T. Ng and D. M. Hercules, *J. Am. Chem. Soc.,* **97,** 4168 (1975).

26. E. T. Kang, H. C. Ti and K. G. Neoh, *Polym. J.,* **20,** 845 (1988).

27. S. R. Mirrezaei, H. S. Munro, and D. Parker, *Synth. Metals,* **26,** 169 (1988).

28. K. L. Tan, B. T. G. Tan, E. T. Kang, and K. G. Neoh, *Phys. Rev. B,* **39,** 8070 (1989).

29. R. Foster, *Organic Charge-Transfer Complexes,* Academic, London, 1969, p. 315.