

degrade after repetitious cycling if the anodic return potential was extended to 1.0V. Under these conditions, the waves due to PV-Fc disappeared, although the film was still on the electrode and the frequency of the QCM did not indicate loss of polymer from the electrode. In addition, the film becomes reddish brown in color under these conditions, suggesting the presence of inorganic iron species, most likely oxides. In the presence of $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ or $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$ the small amounts Fe^{3+} produced by repeated excursions to +0.7V may be trapped to form PB complexes. It should be noted that PB films are generally believed to insert K^+ ions upon reduction in order to maintain electroneutrality (12, 13). However, we have not observed any evidence for an increase in mass upon reduction of these films. If K^+ ion was exclusively involved with the exchanged ferro(ferricyanide) and NO_3^- with unexchanged redox-active PV-Fc sites, a frequency decrease upon oxidation of 80 Hz could occur only if 33% of the film was exchanged. Since the cyclic voltammetry indicated complete disappearance of the PV-Fc waves, this does not seem likely.

Our previously reported RRDE studies indicated that the bimolecular reaction rate of Eq. [1] decreased with increasing $[\text{Fe}^{\text{II}}(\text{CN})_6^{4-}]$. This was attributed to partitioning of the multiply charged anion into the positively charged films, resulting in electrostatic cross-linking and decreased activity of the PV-Fc redox sites. However, the RRDE studies did not indicate the dramatic changes described here since the films in the RRDE investigations were not cycled for prolonged periods and low $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ concentrations were used (<0.5 mM) where exchange was slow. QCM experiments corroborate this behavior as the exchange process was significantly attenuated at lower concentrations; in 0.1 mM solutions, the exchange rate was slower by approximately an order of magnitude. Nevertheless, the exchange phenomenon demonstrates that caution must be exercised when investigating reactions involving these films. It was recently reported that PV-Fc/PV-Fc⁺ films could be used more reliably as reference electrodes in the presence of $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ if the films were extensively cross-linked (14) compared to untreated PV-Fc films (15). Our results suggest that cross-linking

probably may inhibit exchange of ferro(ferricyanide) into the film as well as electron transfer.

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REFERENCES

- (a) N. Oyama and F. C. Anson, *This Journal*, **127**, 640 (1980); (b) N. Oyama and F. C. Anson, *ibid.*, **127**, 247 (1980).
- I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, **102**, 6641 (1980).
- J. R. Schneider and R. W. Murray, *Anal. Chem.*, **54**, 1508 (1982).
- (a) B. Zinger and L. L. Miller, *J. Am. Chem. Soc.*, **106**, 6861 (1984); (b) L. L. Miller, B. Zinger, and Q. X. Zhou, *ibid.*, **109**, 2267 (1987).
- (a) A. N. K. Lau and L. L. Miller, *ibid.*, **105**, 5271 (1983). (b) A. N. K. Lau, B. Zinger, and L. L. Miller, *ibid.*, **105**, 5278 (1983).
- M. D. Ward, *J. Phys. Chem.*, **92**, 2049 (1988).
- R. W. Murray, in "Electroanalytical Chemistry," Vol. 13, A. J. Bard, Editor, p. 191, Marcel Dekker, Inc., New York (1984).
- G. Sauerbrey, *Z. Phys.*, **155**, 206 (1959).
- M. D. Ward, *J. Electroanal. Chem.*, **236**, 139 (1987).
- (a) R. Lange and K. Doblhofer, *ibid.*, **216**, 241 (1987); (b) K. Doblhofer, H. Braun, and R. Lange, *ibid.*, **206**, 93 (1986).
- (a) K. Itaya, I. Uchida, and V. D. Neff, *Acc. Chem. Res.*, **19**, 162 (1986); (b) K. Itaya, T. Ataka, and S. Toshima, *J. Am. Chem. Soc.*, **104**, 4767 (1982).
- D. Ellis, M. Eckhoff, and V. D. Neff, *J. Phys. Chem.*, **85**, 1225 (1981).
- K. Itaya and I. Uchida, *Inorg. Chem.*, **25**, 389 (1986).
- S. M. Kannuck, J. M. Bellama, E. A. Blubaugh, and R. A. Durst, *Anal. Chem.*, **59**, 1473 (1987).
- P. Peerce and A. J. Bard, *J. Electroanal. Chem.*, **108**, 121 (1980).

The Spectroelectrochemical Determination of "Formal Potentials and n-Values" of Some Electrochemically Formed Conducting Poly(heterolene) Films

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ABSTRACT

UV-VIS spectroelectrochemistry has been used to determine the formal potentials and n-values of electrochemically polymerized conducting poly(heterolene) films. Ten polymeric compounds obtained from the monomers with different number of heterolene units, substitutions, and varying number of oxygen and sulfur moieties were studied. Trends for the change of formal potential values vs. the electronic excitation energies were obtained and discussed in several groups of related polymers. The effects of the number of rings and substitutions in monomer units on the spectral and electrochemical behavior of the polymers were investigated.

In recent years, spectroelectrochemistry employing optically transparent electrodes (OTE) has provided novel and convenient means for quantitative examination of electrode processes and determination of "the formal potentials and n-values" of redox systems (1-3). It has been

demonstrated that conducting polymers exhibit changes in their optical spectra in the presence of a dopant depending on the applied potential (4,5). Electrochemically reversible anion incorporation by several conducting polymers has been described (6) and continues to be of interest. The spectroelectrochemical determination of "the formal potentials and n-values" of certain new materials, such as electroactive aromatic poly(imides) has also been reported (7).

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In the present work, electrochemical and spectroelectrochemical approaches have been employed to study the redox chemistry of some electrochemically grown polyheterolene thin films in order to determine their "formal potentials and n -values" and to investigate the possible related effects of certain parameters such as the degree of substitution, number of rings; presence of oxygen in the ring(s) and steric hinderance.

The results presented in this paper constitute a partial extension of our previous studies (8-12). It should be noted that the spectroelectrochemical approach reported here is similar to what was independently reported by Park and his co-workers (13).

Experimental

The starting materials (as listed in Table I) for the polymers studied were synthesized by the coupling of Grignard compounds with the appropriate bromoheterolene (14-17), except for 3-methyl thiophene which was purchased from Aldrich Chemical Company, Milwaukee, Wisconsin. Tetrabutylammonium tetrafluoroborate (TBAFB) was supplied by Southwest Analytical Chemicals, Austin, Texas, and was used as electrolyte. HPLC-grade acetonitrile, water content of 0.02% and an ultraviolet cutoff at 190 nm, was obtained from Fisher Scientific Company, Cincinnati, Ohio, and was kept over molecular sieves Type 4A of Fisher Scientific Company, Cincinnati, Ohio, for at least 48h prior to use as solvent. All the synthesized starting materials and commercially obtained chemicals were used without any further purification. All the studies were conducted in 0.1M TBAFB in acetonitrile.

A PAR Model 173 Potentiostat/Galvanostat mounted with a plug-in PAR Model 176 Current-to-Voltage Converter (Princeton Applied Research, Princeton, New Jersey) and a Model CV-1B Cyclic Voltammetry Unit (Bioanalytical Systems, Incorporated, West Lafayette, Indiana) with a Hewlett Packard Model 7004B X-Y recorder and a Fluke 8000A Digital Multimeter were employed for electrochemical preparations and measurements.

Table I. The list of polymers studied and their starting compounds

| No. | Representative Formula | Name of the Starting Compound |
|-------|------------------------|------------------------------------------------|
| I. | | 3-Methyl thiophene |
| II. | | 2,2'-Bithienyl |
| III. | | 2,2'-Thienyl furan |
| IV. | | 3-Ethyl-2,2'-bithienyl |
| V. | | 3-Ethyl-3'-methyl, 2,2'-bithienyl |
| VI. | | 3,3'-Diethyl-2,2'-bithienyl |
| VII. | | 2,2':5',2''-Terthienyl |
| VIII. | | 4'-Ethyl-3-3''-dimethyl-2,2':5',2''-terthienyl |
| IX. | | 2-2':5',2''':5''-Tetrathienyl |
| X. | | 4H-Cyclopenta(2,1-b:3,4-b')dithiophene |

The spectrometric studies were performed using either a Perkin-Elmer Lambda 5 or a Varian Techtron Model 635 LC UV-VIS spectrometer with a Fisher Recordall, Series 5000 x-t recorder.

The polymeric films were grown galvanostatically using a current density of 2 mA/cm² at room temperature (20°-22°C) and atmospheric medium. Initial concentration of the starting compound was 50 mM, and the duration of electropolymerization was 60s for all the cases. Under the conditions mentioned above, the anode potential attained a constant value. A simple one-compartment glass cell was employed. The working electrode (OTE) on which the films were grown was a high-transmission, 87.0-90.0%T, n-doped tin oxide half-wave coated glass, 1 mm × 8 mm × 40 mm (NESA glass, PPG Industries), with a nominal 50 nm SnO₂ film thickness, provided by Donnelly Corporation, Holland, Michigan. A 35 cm² platinum sheet was used as the auxiliary electrode. All the potential values were referred to a (3M) Ag/AgCl electrode. After synthesis, the films grown on the NESA glass were thoroughly rinsed with solvent and were soaked in batches of fresh electrolyte solution for 15 min before further experiments. The polymer films were cycled repeatedly between -0.2 and +1.1V until a constant voltammogram was obtained, just prior to spectral and/or electrochemical measurements.

A matched pair of 10 mm pathlength rectangular Suprasil cells (160-2600 nm) for spectral use were obtained from Fisher Scientific Company, Cincinnati, Ohio. The OTE was held on a slotted PTFE block fitted at the bottom of the cell mentioned above such that its surface bearing the polymer film was perpendicular to the light beam in the spectrometer. Pt wire auxiliary and (3M) Ag/AgCl reference electrodes were inserted into the same cuvette so as not to interfere with the light beam. The spectral measurements were carried out in double-beam mode where the reference cell contained a matched cuvette with a blank OTE in electrolyte. In the absence of the anolyte, the double-beam configuration gave a flat spectrum indicating that the absorbances by tin oxide-coated glass electrodes were effectively compensated. The applied potential on film was successively increased from 0.0 to about +1.1V with intervals of normally 100 mV; however, after the current started to increase as indicated by the cyclic voltammogram, smaller steps down to 5 mV were employed as required, since the spectral features at this region showed significant changes within such small voltage variations. Following the application of each potential value, absorption spectrum was recorded at the region of 300-760 nm after the equilibrium was reached as indicated by a constant absorbance at a fixed wavelength, conveniently measured at λ_{max} , and a constant current as observed. Near the positive extreme potential values, normally at about +0.9V, fresh batches of electrolyte were used in order to alleviate the effect of soluble and insoluble particles leaving the OTE surface.

Results and Discussion

For the sake of brevity, the roman numerals in Table I representing the polymeric compounds will be used throughout the discussion. All the potential values are vs. Ag/AgCl electrode. "E^o" and n values" have been calculated, using the absorbance values of the reduced species at its λ_{max} , for increasing applied potential by employing the method described elsewhere (2). However, in the present study, the analyte is a solid film in contrast to the cases in literature (1-3) where solution in proximity of the electrode surface was investigated. Initial concentration of the reduced form, R, or the total concentration of the polymer present was found from the absorbance peak value at 0.0V; equilibrium concentration values for both reduced and oxidized forms, R and O, were calculated from the decreasing absorbance value and its difference from the initial total value, respectively, as the potential was successively made more positive. For each polymer, the changes in the background of the absorption band were considered and the absorption measurements were made by drawing a line between the minimum absorbance points at both sides of the peak, and measuring the difference between the peak value and the corrected background.

Table II. λ_{\max} , E° , n-values and colors of the polymers studied

| No. ^a | Reduced form ^c | | | Color ^b | |
|------------------|---------------------------|-----------------|------|---------------------------|----------------------------|
| | λ_{\max} , nm | E° , V | n | Reduced form ^c | Oxidized form ^d |
| I | 510 | 0.62 | 0.30 | dark red | blue |
| II | 484 | 0.92 | 0.30 | red | blue-gray |
| III | 448 | 0.68 | 0.21 | brown | green |
| IV | 475 | 0.90 | 0.30 | red | blue |
| V | 420 | 0.81 | 0.29 | gray-green | blue-violet |
| VI | 413 | 0.78 | 0.52 | yellowish green | blue |
| VII | 356 | 0.85 | 0.23 | pale yellow | orange-red |
| VIII | 375 | 0.78 | 0.42 | pale yellow | orange |
| IX | 340 | 0.79 | 0.23 | yellow | greenish blue |
| X | 550 | 0.43 | 0.32 | brown | black-gray |

^aSame numbers as in Table I.

^bApparent transmitted colors to human eye under white-light illumination on tin oxide-coated glass.

^cThe species at 0.0V vs. Ag/AgCl electrode.

^dThe species at nearly +1.0V vs. Ag/AgCl electrode.

The reduced species at around 0.0V is expected to be in a rather chargeless form. As the applied potential becomes more positive, the polymer gradually acquires a positively charged character; meanwhile, incorporation of the anion(s) present in the solution takes place. Therefore, the reduced and the oxidized species should be regarded as the forms at the two extremes of applied potentials, rather than a physically separable and conventional redox couple. Bearing this statement in mind, the role and the significance of the " E° " and n-values" should be viewed as operational with a rather experimental importance. Where all the experimental conditions are kept similar for each polymeric compound in the series, as in the present study, " E° " and n-values" should serve as very convenient criteria for the comparison of the structural effects such as number of rings, presence of oxygen as the heteroatom, and steric hinderance. Evaluation of the certain trends in any closely related series of polymers can serve as a powerful tool for a better understanding of the chemical and physical behaviors imparted by these compounds. For instance, a relatively positive E° value for a certain species in the series indicates a more unfavorable process for removing electrons and imparting a positive charge to the polymeric compound. The "n-values," on the other hand, represent the experimentally found number of electrons transferred per unit represented by the starting compound.

" E° " and n-values," together with peak wavelengths of the reduced species and the colors of the oxidized and reduced forms, have been presented in Table II. A typical

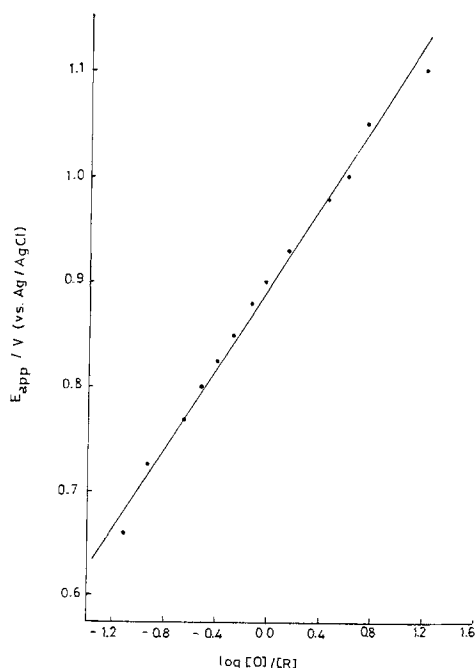


Fig. 1. The plot of applied potential against $\log([O]/[R])$ for poly(3-ethyl-2,2'-bithienyl) film.

plot employed for the calculation of n-values from the slope and E° values from the intercept is illustrated in Fig. 1. Linear regression was used in all the cases, and the correlation coefficients for the lines had a range of 0.962-1.000. Occasionally, at positive potential values near +1.0V, measurement of the absorbance values became relatively difficult owing to the changing and sloping background, yielding scattered results. In such cases, only the values in the region where absorbance of the reduced species changed smoothly were employed. Representative spectra and a cyclic voltammogram for the polymer (IV) are given in Fig. 2 and 3, respectively.

At sufficiently high positive potentials, an elevation of the spectral background was observed for all the cases, as in Fig. 2, g and h. Almost simultaneously, the gradual increase in the anodic current was stabilized as shown in Fig. 3. A visually observed color change accompanied these two events described above when the film was cycled through the same potential range under the same conditions out of the spectrometer using the white light illumination for convenient observation. In the present study, at such high potentials the polymeric films all acquired a grayish color character and became physically more vulnerable such that even the slight vibrations caused partial flaking-off from the surface. In the initial stages of experiments, this behavior presented a nuisance and an important cause of inaccuracy and an irreversible behavior for the film. However, using a fresh batch of electrolyte prior to application of the new potential value has completely eliminated this problem. Accompanied by this improved

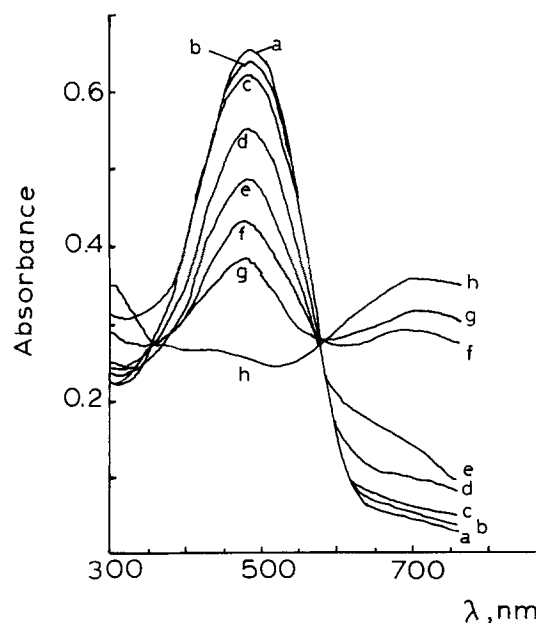


Fig. 2. Absorption spectra of poly(3-ethyl-2,2'-bithienyl) film at various applied potentials: a-0.0, b-0.60, c-0.69, d-0.75, e-0.77, f-0.79, g-0.90, and h-1.1V.

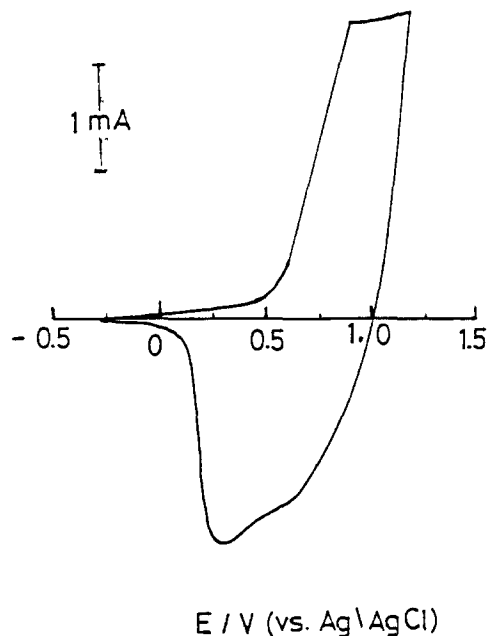


Fig. 3. Cyclic voltammogram of poly(3-ethyl-2,2'-bithienyl) film. Scan rate is 50 mV/S.

physical behavior, the elevation in spectra was significantly reduced. Therefore, on the basis of these observations, such as grayish color and elevation of spectral background, it may be suggested that at sufficiently high positive potentials as the anions in the medium are incorporated into the polymeric films, they cause some morphological as well as chemical changes, possibly resulting in a certain stress in the structure to cause many tiny cracks imparting the gray color analogous to a spectral neutral density filter. While the polaron and bipolaron states should be responsible for some spectral changes (18), the physical effects described above were also found to play a role. When the absorbance values were calculated considering the elevated background, the data points were fairly consistent with the rest of the line for an E_{app} vs. $\log([O]/[R])$ plot. The role of using a fresh electrolyte each time, although not fully understood at this stage, has proved experimentally convenient for the purpose of this study. Similarly, cycling the film several times following its preparation resulted in more reproducible results and denser, more adherent films.

During the synthesis and selection of the polymeric compounds as listed in Table I, formation of meaningful subseries were planned so as to conveniently investigate the effect of certain structural parameters. One such subseries can be evaluated on the basis of the number of thiophene units in the starting compound. It can be observed from Table II that as the number of units increases, the peak wavelength shifts to smaller wavelengths. This trend is the reverse of that given for a related series of starting compounds (15). While this observation by itself may be interesting, it should be remembered that once the polymeric compounds are formed, they are now new species which will not necessarily show the similar trends as those shown by their starting compounds.

Further investigation of the E° values in Table II in relation to the number of rings in the series of starting compounds reveal another trend. As the number of rings increases, E° values become less positive, excluding (I). The averages of E° values for two- and three-member groups, namely, (II), (IV), (V), and (VI), (VII) and (VIII), and a single value for (IX), are 0.85, 0.82, and 0.79V respectively. This behavior is similar to what was reported before (15) where oxidation potentials, obtained by the peak potentials of cyclic voltammograms, showed a decreasing trend with the increasing number of rings in a series of related monomers. In an analogous manner, with the higher number of rings, the delocalization and thus stabilization of the derived radical cations is facilitated, causing less positive E° values in this study. However, it should be noted that the

values above were not found to be significantly different by statistical evaluation and thus more data are required for conclusive statements, since the use of and the decisions by statistical tests are not very meaningful for such small sets.

The effect of oxygen heteroatoms were studied for the first time. When " E° values" from Table II are compared, it can be observed that the polymer (II) which does not contain oxygen has a value of +0.92V, where the polymer (III) with an oxygen atom in one of its rings has a value of +0.68V, less positive than the former. In another study, a similar trend has been found; the increased number of oxygen heteroatoms resulted in lower oxidation potential values for block copolymers from oligomers containing thiophene and furan rings (14).

The investigation on unsubstituted polymers (II, VII, and IX) has shown that as the number of thiophene units in the starting compound increases, higher delocalization possibilities, and thus better conjugation, result in lower E° values. While this is an expected behavior, the decrease in E° values are accompanied by an increase in the electronic transition energies, a trend contrary to some other studies on fused-ring systems (19). A group of polymers with increasing substitution (II, IV, V, and VI) also had decreasing E° values with increasing electronic transition energies. Linear plots of E° values in volts vs. the electronic transition energies in eV, had correlation coefficients of -0.940 and -1.000 for the aforementioned groups of unsubstituted (II, VII, IX) and increasingly substituted (II, IV, V, VI) polymers, respectively. For the group containing the polymers II, IV, V, and VI, the increasing substitution will reduce the degree of conjugation owing to the steric hinderance and lower coplanarity. On the other hand, the positive induction effect also influences delocalization possibilities and prediction on these combined effects becomes difficult.

Another notable observation was a relation between the degree of morphological order and the value of λ_{max} . In the group of II, VII, and IX, the increasing number of the thiophene units in the starting compound results in less orderly, less compact polymerization due to longer oligomers, and successive blue shifts are observed. In the group of II, IV, V, and VI, as the degree of substitution increases, less orderly polymerization is expected owing to steric hinderance and lowered coplanarity, where blue shifts are also observed. As a support for this argument, the λ_{max} value for (X) was found to be 550 nm, showing a considerable red shift compared to the other two-ring compounds. The free rotation is not allowed for the starting compound of (X); therefore, an orderly polymerization is expected, accompanied by a red shift. Although certain trends have been observed, the relationship between the degree of conjugation, electronic transition energy, and E° values are difficult to predict and explain at this stage of the studies.

One noteworthy observation from Table II has been that relatively large n-values were found for the highly strained structures (VI) and (VIII), 0.52 and 0.42, respectively. It may be suggested that in these cases, because of the high steric hindrance and thus low coplanarity among the units, each individual ring has been independently subjected to oxidation, consequently resulting in a high n-value.

Conclusion

In the present work, a spectroelectrochemical approach was employed to study some novel conducting poly(heterole) films. Electrochemistry alone may not be sufficient in many cases as the cyclic voltammograms of some polymer films often show broad waves and very narrow spikes of uncertain origin (12, 20). Employing spectroelectrochemistry along with the electrochemical techniques, useful correlations and trends can be sought regarding the behavior of these polyheterole films. Although the " E° and n-values" obtained in this study are operational terms, the trends obtained should be very useful in behavior characterization of some series. In this study, it has been shown that the poly(heterole) films with various ring numbers, heteroatoms, and substitutions behave differently. These different behaviors can be utilized for several

analytical and/or industrial applications, such as development of novel sensors based on the electrochromic and electrochemical properties of these films. E° values are indicative of the potential ranges in which these films can be used in a reversible manner without being destroyed. The results, and the approach used in this paper can be employed in order to establish strategies for the synthesis of novel conducting polymers which continue to be a significant and challenging area of interest.

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REFERENCES

1. W.R. Heineman, B. J. Norris, and J. F. Goelz, *Anal. Chem.*, **47**, 79 (1975).
2. T. P. DeAngelis and W. R. Heineman, *J. Chem. Educ.*, **53**, 594 (1976).
3. A. J. Bard and L. R. Faulkner, "Electrochemical Methods," pp. 577-583, John Wiley and Sons, Inc., New York (1980); P. T. Kissinger and W. R. Heineman, in "Laboratory Techniques in Electroanalytical Chemistry," W. R. Heineman and P. T. Kissinger, Editors, pp. 64-69, Marcel Dekker, Inc., New York (1984).
4. C. R. Fincher, Jr., M. Ozaki, A. J. Heeger, and A. G. MacDiarmid, *Phys. Rev. B*, **19**, 4140 (1979).
5. B. Tieke, C. Bubeck, and G. Lieser, *Makromol. Chem. Rapid Commun.*, **3**, 261 (1982).
6. "Handbook of Conducting Organic Polymers," Vol. 1 and 2, T. A. Skotheim, Editor, Marcel Dekker, Inc., New York (1986).
7. S. Mazur, P. S. Lugg, and C. Yarnitzky, *This Journal*, **134**, 346 (1987).
8. D. D. Cunningham, H. B. Mark, Jr., H. Zimmer, C.-V. Pham, E. T. Lewis, A. Nkansah, T.-L. Chang, N. Klaus, and L. Laguren-Davidson, 194th American Chemical Society National Meeting, New Orleans, Louisiana, September 1987.
9. H. B. Mark, Jr., H. Zimmer, D. D. Cunningham, C.-V. Pham, E. T. Lewis, A. Nkansah, T.-L. Chang, N. Klaus, and L. Laguren-Davidson, Paper 1616 presented at The Electrochemical Society Meeting (Joint with The Electrochemical Society of Japan), Honolulu, HI, October 18-23, 1987.
10. A. Galal, O. Y. Ataman, E. T. Lewis, L. Laguren-Davidson, D. D. Cunningham, C.-V. Pham, A. Burkhardt, H. Zimmer, and H. B. Mark, Jr., 39th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, Louisiana, February 1988.
11. *Ibid.*
12. D. D. Cunningham, Ph.D. Thesis, University of Cincinnati, Cincinnati, OH (1987).
13. S. N. Hoier, D. S. Ginley, and S.-M. Park, *This Journal*, **135**, 91 (1988).
14. A. Galal, E. T. Lewis, O. Y. Ataman, H. Zimmer, and H. B. Mark, Jr., Submitted to *J. Polym. Sci., Polym. Lett. Ed.*
15. D. D. Cunningham, L. Laguren-Davidson, H. B. Mark, Jr., C. V. Pham, and H. Zimmer, *J. Chem. Soc. Comm., Chem. Commun.*, 1021 (1987).
16. C. V. Pham, R. S. Macomber, H. B. Mark, Jr., and H. Zimmer, *J. Org. Chem.*, **49**, 5250 (1984).
17. Armin Burkhardt, M. S. Thesis, University of Cincinnati, Cincinnati, OH (1987).
18. J. L. Bredas and G. B. Street, *Acc. Chem. Res.* **18**, 309 (1985).
19. E. S. Pysh and N. C. Yang, *J. Am. Sec. Soc.*, **85**, 2124 (1963).
20. L. Laguren-Davidson, Ph.D. Thesis, University of Cincinnati, Cincinnati, OH (1986).

Electromotive Force Measurements in Molten Rb-Bi Alloys with a Rubidium β'' -Alumina Electrolyte

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ABSTRACT

A Rb- β'' -alumina solid electrolyte was developed by the exchange of Na- β'' -alumina in RbCl and was used in concentration cells to measure the activity of Rb in liquid Rb-Bi alloys. Values of ΔG , ΔH , and ΔS are reported for the temperature range 600-883 K. All were highly negative, indicating strong interaction between Rb and Bi in the melt. The excess stability was found to have two peaks, one at the 1:1 composition and the second near the stoichiometric 3:1 ratio. Liquidus points on the phase diagram were measured over most of the composition range.

The group of binary alloys known as "ionic alloys" has received considerable attention in the past decade because of their unusual properties in the liquid state. Their electrical, optical, magnetic, and thermodynamic properties indicate a tendency toward nonmetallic behavior at the 1:1 composition and/or the stoichiometric composition (*i.e.*, at the atomic fraction ratio equal to the ratio of the valences of the elements). The best known example of this group is Cs-Au, but alloys formed by other alkalis with the electro-negative metals Sn, Pb, Sb, Bi, etc., show similar behavior.

The thermodynamic properties of such alloys containing Na and K have been studied electrochemically in the past with glass electrolytes or more recently with β alumina (1, 2). Na- β -alumina is an excellent Na-ion conductor with very low electronic conductivity over a wide temperature range. It has good thermal stability and is chemically inert to most metals. Furthermore, it can be exchanged with other monovalent cations to form, for example, Li-, K-, and Ag-ion conducting electrolytes. Na- β -alumina has also been exchanged to form Rb- β -alumina but in single-crystal form only (3). In the present study we used β'' -alumina, a structural modification of β -alumina, for making poly-

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