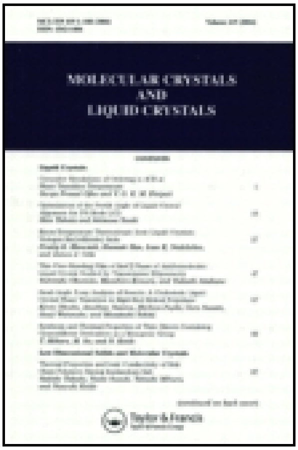

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Evolution of Polaron States Into Bipolarons In Polypyrrole

J. H. Kaufman [a], N. Colaneri [b], J. C. Scott [a], K. K. Kanazawa [a] & G. B. Street [a]

[a] IBM Research Laboratory, San Jose, California, 95193

[b] U.C.S.B. Dept of Physics, Santa Barbara, Ca.

Version of record first published: 17 Oct 2011.

To cite this article: J. H. Kaufman, N. Colaneri, J. C. Scott, K. K. Kanazawa & G. B. Street (1985): Evolution of Polaron States Into Bipolarons In Polypyrrole, Molecular Crystals and Liquid Crystals, 118:1, 171-177

To link to this article: http://dx.doi.org/10.1080/00268948508076206

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 171-177
0026-8941/85/1184-0171/$15.00/0

Printed in the United States of America

EVOLUTION OF POLARON STATES INTO BIPOLARONS IN POLYPYRROLE

J. H. Kaufman, N. Colaneri*, J. C. Scott, K. K. Kanazawa, and G. B. Street

IBM Research Laboratory San Jose, California 95193

*** U.C.S.B. Dept of Physics Santa Barbara, Ca.**

ABSTRACT The kinetics of polaron recombination into bipolarons in polypyrrole have been studied using optical absorption spectroscopy on films doped *in situ* in an electrochemical cell. ESR studies confirm that the metastable states possess spin, while the stable states do not. We also report the development of a new electrochemical technique which indicates charge is stored at two localized energy levels in the gap. The optical and ESR data both reveal a slow evolution, consistent with polaron diffusion rates limited by the mobility of the accompanying counterion.

The observation of high conductivity without ESR absorption[1] in oxidized polypyrrole (PP) films and characteristic optical absorption[2] demonstrate the importance of bipolaron states in this non-degenerate ground-state polymer.[3,4,5] Bredas *et al.*[6] have shown through band structure calculations on a deformable polypyrrole chain that both polaron and bipolaron formation is possible on the polymer lattice. Since injection of single charges, for example in electrochemical doping, can only result in polaron formation,[7,8,9] a strong test of the bipolaron description in this class of materials would be the direct observation of polaron recombination into bipolarons. In this paper, we report the results of optical and ESR experiments which probe the kinetics of this process.

In-situ opto-electrochemical techniques[10] have been used to measure the optical absorption as a function of degree of oxidation (determined by applied voltage) and time. The data reveal electronic states at the predicted[6] polaron energies even at high doping levels. These states evolve with time into electronic levels at predicted bipolaron energies (see Fig. 1) . The evolution takes place on time scales typical of mass transport rates, suggesting a novel process wherein diffusion of the counterion is the limiting step in the electronic reaction

$$P^{+}_{1/2} + P^{+}_{1/2} \rightarrow B^{++}_{0} + \text{phonons} \qquad (1)$$

where the subscripts indicate the spin of each species. Parallel *in-situ* ESR-electrochemical experiments reveal a spin signal which appears for a comparable time after changing the oxidation state of the polymer.

Polypyrrole films were prepared by electrochemical polymerization under drybox conditions as described elsewhere.[11] These films may be repetitively reduced and reoxidized electrochemically. Samples were prepared on conducting (indium-tin oxide coated) glass at current densities of 0.2 mA/cm^{-2}. for ~10 min. The films obtained were ~2000Å thick based on a density of 1.48 g/cm^{4},[12] a ratio of 2.3 electrons per pyrrole unit,[11] and known film area.

It is important to consider the consequences of the non-degenerate ground state of the polypyrrole chain.[3] Removal of a single electron from the chain, accompanied by a lattice relaxation, generates a polaron. Polaron states in the band gap result in three allowed optical transitions (Fig. 1) below the interband transition.[4] In the absence of Coulomb correlations, the sum of the two lowest absorption energies should equal the third. Subsequent removal of electrons may lead to more polarons, or, if pairing of charges is energetically favorable and kinetically achievable, to bipolarons. Soliton formation is prohibited because the creation of two domain walls on a chain results in a region of higher energy between the two charged sites. As a result, charged defects are bound together as bipolarons (stabilized dications). Bipolaron states in the gap result in only two allowed subgap transitions since the electronic states are either both occupied or, as in the case of polypyrrole which can only be oxidized,[11] both empty.[4]

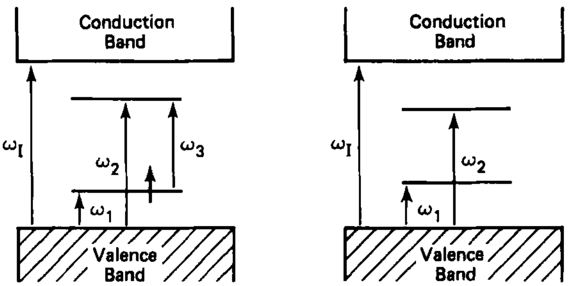

Figure 1. (a) Energy level diagram for a polaron state showing allowed optical transitions, ω_1,ω_2 and ω_3. ω_I is the interband threshold. (b) Same for bipolaron state. Note the absence of transition ω_3.

Previous optical measurements at high doping levels by Yakushi *et al.*[2] reveal two intense absorptions within the PP gap. These have been attributed to the transitions from the valence band into the two wide bipolaron bands which are formed upon doping. At very low dopant concentration, three peaks are observed and explained in terms of polaron states. In this case there is an additional allowed transition, from the occupied lower (bonding) polaron level to the unoccupied antibonding state.

Figure 2 shows the opto-electrochemical data for reduction of polypyrrole film from the oxidized (as grown) state to near neutral. The technique is described elsewhere.[7,10] The cell is never moved in the course of the experiment. At high doping levels, the spectra reveal absorption maxima at 0.70 eV and 2.30 eV (±0.01 eV) with the interband at 3.20 eV. (Fig. 2, a-d)

The data in Fig. 2 are in good agreement with the predicted optical absorption features for bipolarons. The sum of the two absorption energies corresponds approximately to the interband edge at 3.00 eV. The lower energy absorption is more intense, and at higher dopant levels, the interband transition shifts to higher energy. The data demonstrate that the transition, at 1.18 eV between localized polaron levels is observable even at high concentrations when equilibration times (after displacing the cell from equilibrium potential) are kept small. Spectra b, c, f, and g were taken at 1/2 hr or less after stepping the applied voltage. In the dilute doping regime (f and g), the absolute intensity of the polaron feature increases, as doping level decreases - the extra oscillator strength coming from the bipolaron signatures.

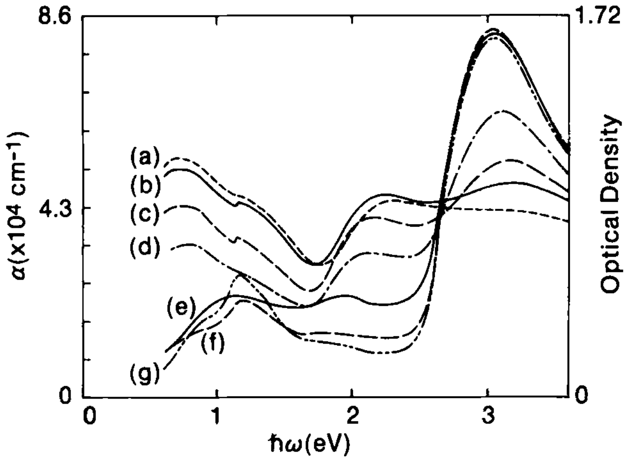

Figure 2. Sequence of optical spectra of polypyrrole taken during reduction, at various times after a voltage step in the electrochemical cell; a: 2.98V 1hr.,b: 2.90V 30min.,c: 2.80V 30min.,d: 2.75V 12hr., e: 2.70V 12hr., f: 2.40V 30min., g: 2.20V 30min. The corresponding dopant concentrations are 20,15,11,9,5,2,0.5 mole percent, respectively.

Spectra taken after 1 hr (curves a and d) show attenuation of the polaron feature which appears only as a shoulder to the lower energy bipolaron absorption. Spectrum e, 12 hr after stepping the voltage, reveals *only* bipolarons in the band gap.

Successive spectra over a narrower range below 1.80 eV were taken as a function of time at fixed voltage. The data in Fig. 3 demonstrate this evolution at low doping (2.2 volts *versus* Li). Spectrum 3a was obtained in equilibrium at 2.4 volts; the potential was then stepped to 2.2 volts and spectra 3b-e taken after times of 40 min., 1h20, 4h35, and 15h45. Initially (3b) the intensity of the bipolaron feature at 0.8 eV decreases, while the polaron (1.2V) absorption shows a relatively small change. By the time spectrum 3c was taken, current had virtually stopped flowing, and the continued evolution of the spectrum reflects the redistribution of charges already present in the sample. After the initial increase of polaron to bipolaron ratio (3a - 3b,c), the entire midgap absorption profile decreases in intensity (3d,e). Recall that polaron states lead to upper (ω_3) and lower (ω_1) transitions at energies very similar to the bipolaron transitions. Then the marked reduction in absorption at the uniquely polaron peak (ω_2 = 1.2eV), and the relatively smaller decrease at 0.8 eV after 15 hrs, demonstrate the recombination of polarons into (half as many) bipolarons.

In order to demonstrate that the species created during charge injection or removal have the spin properties expected for polarons, we constructed an electrochemical cell which could be operated in the cavity of an ESR spectrometer. Each time the voltage across the cell was changed, the spin intensity was observed first to increase, and then to decay on a time scale of order 10^3-10^4 sec. Quantitative details of this experiment are presented elsewhere in these proceedings.

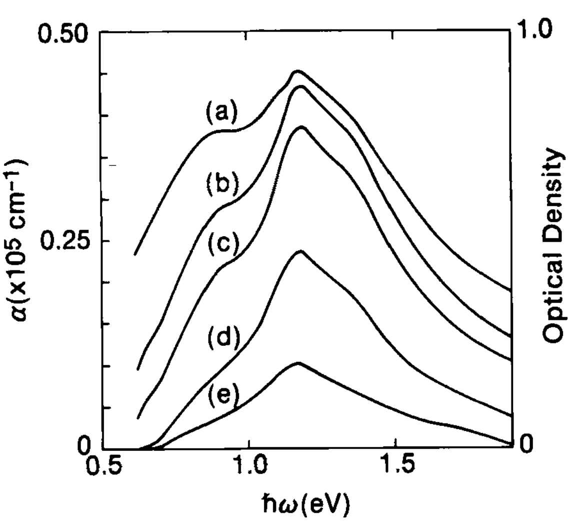

Figure 3. Successive spectra over the limited range 0.62eV to 2.0eV at various times after a voltage step from 2.40V to 2.20V; a: in equilibrium at 2.40V, b: 40min. after step, c: 1hr.20min., d: 4hr.35min., e: 15hr.45min.

The creation of singly charged polaron states by removal or addition of electrons is expected on the basis of simple ideas of electrochemistry, and the subsequent recombination of free polarons to form bipolarons is a natural consequence of the non-degeneracy of the polypyrrole ground state. However, the fact that these reactions can be observed with optical measurements, and that the latter proceeds at rates characteristic of ionic diffusion, is a novel phenomenon in semiconductor physics. It should be noted that this behavior is not observed in similar non-degenerate ground state polymers such as poly(β,β'-dimethylpyrrole) (PβDMP).[13] This may be understood in terms of the degree of structural order of the different materials.[14] For PβDMP,[15] and probably PP, the average chain length is many times the spatial extent of a bipolaron (~4 rings).[6] However, even if a chain can accommodate a large number of polarons, the defects must be close enough (within ~4 rings) for interaction to occur and/or the mobility along the chain must be high. Alternatively, a polaron can hop to a neighboring chain if the chain (and target polaron) are sufficiently close. The probability of both of these processes depends on structural order (density and perfection of chains). Okuno and Onodera[16] demonstrated that, in the Takayama-Lin-Liu-Maki[17] continuum model, a polaron can move through a soliton with no cost in energy. If this argument carries over to the passage of polarons through bipolarons, then polarons formed on long highly ordered chains will recombine rapidly by the nonadiabatic reaction, eqn. 1. Materials less well ordered and with characteristically short conjugation lengths may exhibit polaron trapping - requiring polaron hopping for recombination to occur. If the distance a polaron must travel (or hop) is large, then the rate of polaron recombination is limited by diffusion of the accompanying anion. In polypyrrole, this diffusion rate is slow enough for optical and ESR observation of the polaron species.

To further test for the existence of two levels for charge storage in the polypyrrole band gap we conducted an electrochemical study of the polymer. Electrochemical Voltage Spectroscopy is a convenient way to determine the precise energies at which charge is injected into, and stored in the polymer. We have modified the technique using one contact of a quartz resonator as substrate for the polymer working electrode in an electrochemical cell. Since the resonant frequency of the quartz is proportional to the mass of the polymer, it is possible to determine the mass changes associated with electrochemical currents. The Gravimetric Electrochemical Voltage Spectroscopy (GEVS) data shown in Fig. 4 is analogous to an infinitely slow cyclic voltammogram. The data clearly show charge injection, and storage, at two localized energy levels. Though we have not as yet shown that one of these levels is associated with spinless carriers (and one with carriers possessing spin), one would expect to find charge removal at two energy levels in the gap if charge storage is split between polaron and bipolaron states.

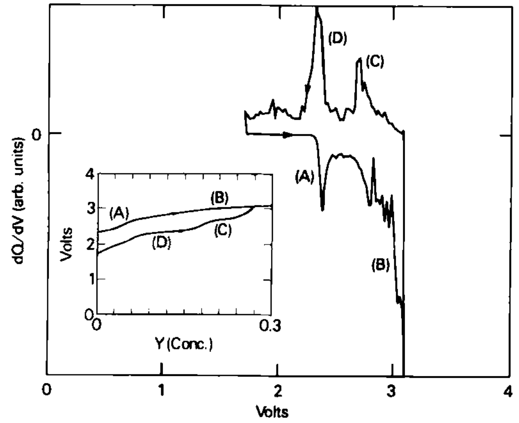

Figure 4. The GEVS data dQ/dV *vs* V reveals the existence of two oxidation and two reduction waves (levels) in the electrochemical cycle of polypyrrole.

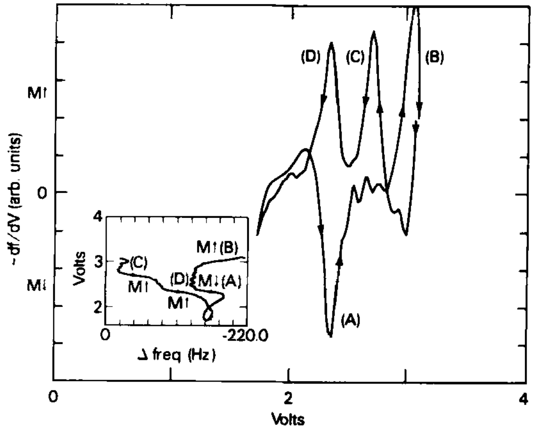

Figure 5. The GEVS data -df/dV ($\propto$ dm/dV) *vs*. V reveals peaks in the differential mass transport at the same energies as the charge transport in fig. 4. Note that reduction of polypyrrole(ClO_4) is associated with a mass *increase*, while the first oxidation peak is associated with a mass *decrease* (see text).

The GEVS data in fig. 5 reveals mass changes at precisely the same energies that charge is transported in fig. 4. However, careful inspection reveals that the peaks corresponding to reduction of the polymer are associated with a decrease in mass, while oxidation of the polymer is associate first with a mass decrease, and at higher energy (above 3.0 volts)with a mass increase. Similar behavior has been observed for PP(BF_4), while PP(toluenesulfonate) exhibits a more intuitive mass decrease upon reduction and increase upon oxidation. We believe the most likely explanation for this behavior is that because perchlorate is a small anion -likely to ion pair - it is tightly bound to the cation of the polymer. During reduction of the oxidized material, charge neutrality is maintained by bringing the more mobile Li cation into the film. During reoxidation, any lithium in the film (as $LiClO_4$) is removed (hence a weight loss is observed). Continued reoxidation, however, necessitates the addition of perchlorate. This explains the weight uptake above 3.0 volts.

In summary, we have shown that electrochemical oxidation or reduction of polypyrrole gives rise, initially, to an excess concentration of polarons. The evolution of the optical spectrum and ESR intensity, after charge injection, demonstrates the recombination of polarons into bipolarons, on a time scale of several hours. This slow process is consistent with the time required for ionic (mass) transport, and therefore we believe that counterion diffusion is the kinetically limiting step in polaron recombination, and that thermodynamic equilibrium is not achieved during the observation time of several hours.

Acknowledgments: This work was supported in part by DOE and by ONR. We wish to thank Prof. A. J. Heeger for use of equipment and for many helpful discussions.

REFERENCES

1. J. C. Scott, P. Pfluger, M. T. Krounbi and G. B. Street, Phys. Rev. B 28, 2140 (1983).
2. K. Yakushi, L. J. Lauchlan, T. C. Clarke and G. B. Street, J. Chem. Phys. 79, 4774 (1983).
3. S. A. Brazovskii and N. N. Kirova, JETP Lett. 33, 4 (1981).
4. K. Fesser, A. R. Bishop and D. K. Campbell, Phys. Rev. B 27, 4804 (1983).
5. J. L. Brédas, R. R. Chance and R. Silbey, Phys. Rev. B 26, 5843 (1982).
6. J. L. Brédas, J. C. Scott, K. Yakushi and G. B. Street, Phys. Rev. B (in press).
7. T.-C. Chung, J. H. Kaufman, A. J. Heeger and F. Wudl, (unpublished).
8. J. H. Kaufman, T. C. Chung and A. J. Heeger, J. Electrochem. Soc. (in press).
9. G. B. Street, in *Handbook of Conducting Polymers,* edited by T. Skotheim, (Marcel Dekker, New York, 1984) (in press).
10. A. Feldblum, J. H. Kaufman, S. Etemad, A. J. Heeger, T.-C. Chung and A. G. MacDiarmid, Phys. Rev. B 26, 815 (1982).
11. G. B. Street, T. C. Clarke, R. H. Geiss, V. Y. Lee, A. Nazzal, P. Pfluger and J. C. Scott, J. Phys. (Paris) Colloq. 44, C3-599 (1983), and references therein.
12. R. H. Geiss, G. B. Street, W. Volksen and J. Economy, IBM J. Res. Devel. 27, 321 (1983).
13. K. Yakushi, J. L. Brédas, L. J. Laughlan and G. B. Street, (unpublished).
14. P. Pfluger, G. B. Street, J. Chem. Phys. 80, 544(1984).

15.; G. B. Street and A. Nazzal, J. C. S., Chem. Commun. 1984, 83.

16. S. Okuno and Y. Onodera, J. Phys. Soc. Japan 52, 3495 (1983).
17. H. Takayama, Y. R. Lin-Liu and K. Maki, Phys. Rev. B 21, 2388 (1980).