

This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 20 February 2013, At: 12:43

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

Epr Study of Polarons In a Conducting Polymer With Nondegen-Erate Ground States: asF₅ Complexes of Poly(p-phenylene)

L. D. Kispert^a, J. Joseph^a, G. G. Miller^b & R. H. Baughman^b

^a Department of Chemistry, The University of Alabama Tuscaloosa, Alabama, 35486, USA

^b Polymer Laboratory Allied Corporation, Morristown, New Jersey, 07960, USA

Version of record first published: 17 Oct 2011.

To cite this article: L. D. Kispert, J. Joseph, G. G. Miller & R. H. Baughman (1985): Epr Study of Polarons In a Conducting Polymer With Nondegen-Erate Ground States: asF₅ Complexes of Poly(p-phenylene), *Molecular Crystals and Liquid Crystals*, 118:1, 313-318

To link to this article: <http://dx.doi.org/10.1080/00268948508076231>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan,

sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

EPR STUDY OF POLARONS IN A CONDUCTING POLYMER WITH NONDEGENERATE GROUND STATES: AsF_5 COMPLEXES OF POLY(p-PHENYLENE).

L. D. KISPERT and J. JOSEPH
Department of Chemistry, The University of Alabama
Tuscaloosa, Alabama 35486 USA

G. G. MILLER and R. H. BAUGHMAN
Polymer Laboratory
Allied Corporation, Morristown, New Jersey 07960 USA

ABSTRACT EPR measurements of temperature-dependent susceptibility and linewidth are reported for poly(p-phenylene) as a function of exposure time to dopant. Most of the charge is in bipolarons, rather than in the spin-associated polarons. Observed decreases in high temperature spin concentration as a function of doping time and post-doping anneal likely arise from both polaron-polaron reaction and polaron ionization to form bipolarons. The susceptibility of all the investigated AsF_5 -doped samples strongly deviate from Curie-Weiss behavior at low temperatures. The observed temperature dependence can be explained by the low-temperature condensation of isolated polarons to form intermolecular polaron pairs in singlet ground states. The interaction between spins is antiferromagnetic and the energy of the singlet-state polaron pair relative to two isolated polarons (-2.4 to -4.8 meV) is similar to that for the n-doped polymer (-2.4 to -2.7 meV).

INTRODUCTION

EPR measurements have been used to characterize electronic states relevant for carrier transport in alkali-metal-doped poly(p-phenylene), (PPP), fully deuterated PPP, and phenylene oligomers. Previous theoretical^{2,3,4} and experimental studies⁵⁻⁷ of AsF_5 - and SbF_5 -doped PPP have suggested the formation of bipolarons (doubly-charged, spinless cations) at high doping levels. From EPR measurements on alkali-metal doped PPP we observed the unpaired spin concentration to be much less than the amount of alkali metal dopant, further suggesting that much of the charge on the polymer chains is in bipolarons. Although g values and linewidths were studied as a function of temperature, the most interesting result is that the measured spin susceptibilities have a temperature

dependence which is not Curie-Weiss over the entire temperature range 7 to 300 K. This can be explained by an equilibrium between separated polaron defects (radical anions, doublet state) and singlet and triplet states formed intermolecularly via polaron pairing. The energy separation (E) between the ground-state singlet and the doublet state calculated from the data for Li, Na, K, and Rb doped PPP varies surprisingly little, from -2.4 to -2.7 meV. Larger variations in E for similarly doped, deuterated PPP (-2.2 to -3.3 meV) might reflect the lower molecular weight of the deuterated PPP and the neglect of chain length effects in the theory. For simplicity in these calculations, the triplet state was assumed to lie $-E$ above the doublet state. However, this assumption is unimportant because relatively few spins are involved in the triplet state at any temperature. At low temperatures, antiferromagnetic spin-spin interactions favor spin pairing in the singlet state rather than the triplet state, and at high temperatures entropy effects favor predominance of isolated spins. Hence, an equally good fit to the experimental data results if the energy of two coupled polarons in the triplet state is higher in energy than two isolated polarons by any energy greater than $-E$. No triplet state is detected by EPR even at low temperature (5-10 K). The absence of measurable triplet states can be due either to their low concentrations or the presence of strong spin exchange.⁸

We have extended our EPR study to include AsF_5 -doping of PPP. Of special interest is whether or not this p-doped polymer shows a similar temperature dependence of susceptibility as we have found for the n-doped polymer.

EXPERIMENTAL

PPP as a powder was taken from the sample preparation used previously for the alkali-metal doped samples.¹ Four different PPP samples were doped with AsF_5 for varying time periods. The exposure time to AsF_5 was five minutes for sample A, 24 hours for sample B, 24 hours for sample C (followed by room temperature storage under argon for six weeks), and four days for sample D. All samples were exposed to excess AsF_5 during the doping period and then evacuated. Except for sample C, all samples were stored in vacuo. The measured dc conductivity (four-probe method) of sample C at the end of the 6-week storage period was 30 S/cm, and the elemental analysis was 19.1% As, 29.31% F, 47.10% C, and 3.92% H, which corresponded to $\text{C}_6\text{H}_{5.95}(\text{AsF}_6)_{0.39}$. The location of the excess hydrogen compared with that for the parent polymer (C_6H_4 theoretical for the infinite polymer and $\text{C}_6\text{H}_{3.7}\text{Cl}_{0.059}$ observed) is unknown, but probably is associated with dopant-derived species. Since the investigated AsF_5 -doped samples did not evidence Curie-Weiss behavior at low temperatures, measurements on another doped PPP sample were used to establish both that the deviations from Curie-Weiss is not an artifact and that Curie-Weiss behavior is

obtainable for other samples of PPP. Specifically, χ was measured for a sample of K-doped PPP which had been heated to 400°C at $5^\circ\text{C}/\text{min}$ in an argon atmosphere. Such thermal treatment degrades the complex, resulting in a dramatic decrease in electrical conductivity. This material exhibits an EPR spectrum which is stable in air for at least several weeks and is quite different from that for the unannealed complex. The measured spin concentration for sample E is 0.009 spins/per phenyl (about equal to that of the AsF_5 -PPP sample D), the conductivity is $7 \times 10^{-8} \text{ S/cm}$, the elemental analysis provides $\text{C}_{6.94}\text{H}_{5.94}\text{K}_{0.082}$, and the EPR linewidth is 4.9 G at 300 K, broadening to 6.55 G at 9.1 K. While this material is not highly conducting, in contrast with the AsF_5 -doped PPP and the unannealed K-PPP, it does have a similar spin concentration to that for the highly conducting complexes. Details of the EPR measurements are given elsewhere.¹

RESULTS AND DISCUSSION

In Table I are listed the experimentally observed number of Curie spins at room temperature for samples A, B, C, D and E, along with

Table I. EPR Data for Samples A, B, C, D and E.

| Sample | Curie Spins Per Phenyl (50 K) | Linewidth (Gauss) | | | A/B (300 K) |
|--------|-------------------------------------|-------------------|------|------|--------------------|
| | | 300 K | 50 K | 8K | |
| A | ---- | 0.90 | ---- | ---- | 3.5 ^(a) |
| B | 0.041 | 2.46 | 2.46 | 2.3 | 2.0 ^(a) |
| C | 0.020 | 7.37 | 6.56 | 6.50 | 1.2 ^(b) |
| D | 0.004 | 3.60 | 3.60 | 3.60 | 2.0 ^(a) |
| E | 0.009 | ---- | 5.32 | 6.65 | ---- |

(a) Sample consisted of a mixture of particle sizes (200–600 μ).
 (b) $\sigma = 30 \text{ S/cm}$. Particle size (50–100 μ) was smaller than that for the other samples.

the Dysonian peak-to-peak linewidth at 300 K, the A/B ratio at 300 K, and the Lorentzian linewidths at 50 and 8 K. All AsF_5 -doped samples exhibited a Dysonian line shape at 300 K which changed to Lorentzian and slightly narrowed or was linewidth invariant as the temperature decreased.

The experimental results obtained on sample A are qualitatively similar to those reported at this conference by Maurice *et al.*⁹ Below 50 K, the EPR spectrum consists of two components, a narrow line ($\Delta H_{pp} \sim 0.5 \text{ G}$) and a broader line ($\Delta H_{pp} \sim 1 \text{ G}$). The presence of two components was attributed⁹ to diffusive and less mobile spins. The narrow-line component was not observed in samples B, C and D.

The observed spin concentrations (Table I) are all much higher than those observed in the undoped polymer (about 2.5×10^{-3} spins/phenyl), and the room temperature linewidth of the undoped polymer (4 - 5 G)¹ is in the range of linewidths observed for the polymer complexes (0.9 - 7.4 G). With increasing doping time (sample A to sample B to sample D), the radical concentration decreases. This is expected since polarons (radical cations) created by the initial doping process can annihilate in pairs to form lower energy bipolarons (spinless), and these polarons can also be ionized by additional dopant to form bipolarons. In the series, sample A to sample B to sample D, the linewidth increases with decreasing radical concentration, as is expected for decreased spin exchange with decreasing spin concentration. An exception to this correlation is that of sample C, which differs from sample B in having been annealed at room temperatures for six weeks. The two-fold decrease in radical concentration during the anneal might result from the known dopant-induced increase of chain conjugation length,¹⁰ which permits recombination of isolated polarons to form bipolarons. The dependence of A/B ratio upon doping time and sample annealing is not directly interpretable in terms of conductivity changes of the samples since this ratio depends upon the ratio of skin depth to particle dimension. This aspect is important, since doping is likely to be nonuniform at short doping times and the present doping process tends to aggregate small particles to make larger particles. Larger particle aggregates were physically removed in order to formulate sample C, which has a d.c. conductivity of 30 S/cm and the smallest A/B ratio.

As we have previously done for the alkali-metal complexes of PPP, the temperature dependence of the susceptibility was analyzed using equations we have derived assuming an equilibrium between isolated polarons and polaron pairs in singlet or triplet ground states.¹ If the enthalpy changes in combining two isolated polarons to make a polaron pair in singlet state is E and the corresponding enthalpy change to make a polaron pair in triplet state is $-E'$, then

$$X = \frac{g^2 \beta^2}{4kT} [R + 2R^2 Z \exp(E'/kT)] \quad , \quad (1)$$

where R is the concentration of unpaired polarons and Z is the number of energetically equivalent positions a polaron can be located on any of the neighboring chains in order to form a singlet or triplet two-polaron state. The concentration of unpaired polarons in Eqn (1) is given by

$$R = \frac{\{1 + 2NZ[1 + 3 \exp((E + E')/kT)] \exp(-E/kT)\}^{1/2} - 1}{Z[1 + 3 \exp((E + E')/kT)] \exp(-E/kT)} \quad , \quad (2)$$

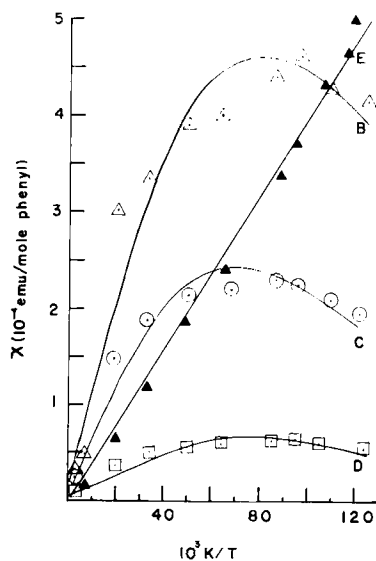
where N is the total concentration of polarons. These equations differ from those in reference 1 only in the generalizations that E' is not required to equal E . The symbol E replaces the previous-

ly used symbol J in order to clarify that E contains both magnetic and electrostatic contributions.

For reasons mentioned in the discussion of the results for alkali-metal complexes, the concentration of triplets is relatively unimportant for the analysis of susceptibility as a function of temperature. This is because both E and E' are negative (antiferromagnetic interaction) and $|E'| \geq |E|$. The latter is true since we can approximate $E = J + E_c$ and $E' = J - E_c$, where J arises from the magnetic interaction and E_c (positive) corresponds to the Coulomb repulsion between polarons.

The comparison between observed and calculated spin susceptibilities for samples B, C, D, and E are shown in Figure 1. Sample E shows Curie-Weiss behavior. Calculated susceptibilities for samples A, B, C, and D (solid lines in Fig. 1) were obtained from Eqns. 1 and 2 assuming E' is infinite. Equally good fits result if $E' = E$. Since Z corresponds to energetically equivalent positions of polarons in pairs, this parameter was constrained to be an integer between 2 and 12. However, both the agreement with experiment and the calculated energy E is not very dependent upon Z . Best agreement was obtained for Z values of 4 or 6 for sample A, 12 for samples B and C, and 2 or 4 for sample D. The calculated E values for samples A, B, C, and D were -2.4, -2.9, -3.6, and -4.8 meV. The number of spins (both isolated and paired) per phenyl calculated from Eqns. 1 and 2 are roughly consistent with the results in Table I that are derived from the observed susceptibility at 50 K. The radical concentrations are: Sample A (0.082), sample B (0.037), sample C (0.019), and sample D (0.003).

Figure 1 χ vs $1/T$ for AsF_5 -doped PPP [sample B(Δ), C(\circ), D(\square)] and for potassium-doped PPP heated to 400°C in an argon atmosphere [sample E(\blacktriangle)]. The solid curved lines are χ calculated from Eqns. (1) and (2) for samples B, C and D.



We conclude from these results that the low-temperature condensation of isolated polarons to form polaron pairs, predominantly in singlet states, can explain the temperature dependence of susceptibility in the AsF_5 -doped PPP samples. The interchain coupling between polarons is antiferromagnetic, and, according to this analysis, the energy difference between isolated polarons and polarons coupled to form a singlet state in the AsF_5 -doped complexes is between -2.4 meV and -4.8 meV. This energy is about the same magnitude as we derived for the alkali-metal complexes of PPP (-2.4 to -2.7 meV).

This work was supported in part by the United States Department of Energy (Office of Basic Energy Sciences). This is DOE Document OR0-4062-90. We thank Rita Hogan for the analytical work.

REFERENCES

1. L. D. Kispert, J. Joseph, G. G. Miller and R. H. Baughman, J. Chem. Phys., **81**, 2119 (1984).
2. J. L. Bredas, R. R. Chance, and R. Silbey, Mol. Cryst. Liq. Cryst., **77**, 319 (1981).
3. J. L. Bredas, R. R. Chance, and R. Silbey, Phys. Rev. B, **26**, 5843 (1982).
4. R. R. Chance, J. L. Bredas, and R. Silbey, Phys. Rev. B, **29**, 4491 (1984).
5. G. Crecelius, M. Stamm, J. Fink and J. J. Ritsko, Phys. Rev. Letters, **50**, 1498 (1983).
6. J. Fink, G. Crecelius, J. J. Ritsko, M. Stamm, H. J. Freund and H. Gonska, J. de Phys., Coll. C3, **44**, 741 (1983).
7. M. Peo, S. Roth, K. Dransfeld, B. Trieke, J. Hocker, H. Gross, A. Grupp and H. Sixl, Solid State Commun., **35**, 119 (1980).
8. J. P. Lloyd and G. E. Pake, Phys. Rev., **92**, 1576 (1953).
9. F. Maurice, C. Fontaine, A. Morisson, J. Y. Goblots and G. Froyer, International Conference on Low-Dimensional Synthetic Metals, Abano Terme, Italy, June 17-22, 1984, Abstr. 89, p. 85.
10. L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, Synth. Met., **1**, 307 (1980).