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

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Version of record first published: 20 Apr 2011.

To cite this article: Lowell D. Kispert , Joy Joseph , Michael K. Bowman , Gerard H. Van Brakel , Jau Tang & James R. Norris (1984): Electron Spin Echo Studies of Donor-Doped Poly(P-Phenylene) and Its Oligomers, Molecular Crystals and Liquid Crystals, 107:1-2, 81-90

To link to this article: http://dx.doi.org/10.1080/00268948408072075

Mol. Cryst. Liq. Cryst. 1984, Vol. 107, pp. 81-90
0026-8941/84/1072-0081/$18.50/0

Printed in the United States of America

ELECTRON SPIN ECHO STUDIES OF DONOR-DOPED POLY(p-PHENYLENE) AND ITS OLIGOMERS

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Abstract Electron spin echo (ESE) measurements for T_1 and T_m were obtained from 4-300 K for potassium and lithium-doped poly(p-phenylene), (PPP), and potassium-doped p-sexiphenyl (6ϕ) and p-terphenyl (3ϕ). At 300 K, $T_1=T_m$ for K-PPP; $T_1=2T_m$ for K-6ϕ and $T_1=10T_m$ for K-3ϕ at the highest possible concentration of donor dopant. T_1 and T_m are temperature independent between 4 and 50 K and vary by a factor of less than four between 4 and 300 K. The temperature independence of T_1 and T_m, and $T_1=T_m$ is attributed to exchange narrowing between anions located on neighboring chains with r<10 Å and not to charge carriers of conductivity.

INTRODUCTION

When potassium naphthalide in dry THF is reacted with poly(p-phenylene), (PPP), $(-C_6H_4-)_n$, n≃16, in an inert atmosphere, the conductivity of the normally insulating polymer increases 12 orders of magnitude, giving rise to a measured conductivity of 7 S/cm.[1-3] Similar doping of p-sexiphenyl, p-quaterphenyl and p-terphenyl gives rise to a measured conductivity of 0.5 S/cm, 2×10^{-5} S/cm and 4×10^{-5} S/cm, the conductivity decreasing with decreasing chain length. Continuous wave (cw) EPR measurements have shown that the charge carriers in doped polyacetylene have a spinless nature and are consistent with the proposed soliton and polaron conduction mechanisms.[4] In the case of PPP, it has been calculated[5] that polaron (radical cation or anion) and bipolaron (dianion or dication) may be the spin-

carrying and spinless charge carriers. Currently, considerable interest exists in proving/disproving these possibilities.

Recent EPR measurements of K-doped PPP shows that an intense Lorentzian line with a peak-to-peak first derivative linewidth of 1.9 G at 300 K occurs due to an unpaired spin concentration equal to approximately 5% of the potassium concentration.[6] A Dysonian lineshape typical for conducting material with dimensions exceeding skin depth is not observed unless the finely divided powder of the K-PPP complex is compressed into pellets. The powder is produced by the preparation in THF. However, EPR studies have now suggested[6] that the measured unpaired spins are not the carriers of the conductivity. In an effort to measure the dynamics of the spin system giving rise to the narrow line, electron spin echo measurements were carried out from 3.7 to 300 K for potassium- and lithium-doped poly(p-phenylene) (K-PPP and Li-PPP), K-doped p-sexiphenyl (K-6ϕ) and K-doped p-terphenyl (K-3ϕ) as a function of dopant concentration. Both phase memory time (T_m) and spin lattice relaxation time (T_1) were measured. Phase memory time is similar to T_2.

EXPERIMENTAL

Poly(p-phenylene) was prepared according to the method of Kovacic et al.[7] and elemental analysis showed the sample to contain 1.8% Cl. Potassium and lithium were obtained from Alfa and had a purity of 99.9%. p-Terphenyl was Kodak scintillation grade and p-sexiphenyl was from Allied Corp. Doping of PPP was carried out using the same apparatus and method employed previously[8] for sodium-doped polyacetylene. Because of the solubility of terphenyl in THF, a weighed quantity of the oligomer and potassium (0.3 K/phenyl) were stirred together vigorously for 24 hours following closely the procedure in Ref. 3. All materials were handled in an inert atmosphere dry box.

EPR measurements were carried out using an X-band EPR spectrometer described previously.[6] A calibrated thermocouple was attached to each sample above the EPR cavity. An NBS Ruby standard was used to calibrate the absolute unpaired spin concentration. Low microwave power (1-5 microwatts) and 270 Hz field modulation were used. The ESE spectra were obtained on the ESE spectrometer described previously.[9]

RESULTS

In Table I are given the unpaired spin concentration per phenyl as a function of dopant concentration determined by C, H and alkali metal analysis.[6] Typically for heavily

Table I. ESR Measurements of T_1 and T_m

Sample[(a)]	Spins per phenyl[(a)]	T_m[(b)] (10^{-6}s)	T_m[(b)] (10^{-6}s)
K-PPP $C_6H_{4.20}K_{0.388}$	0.02_0	0.13	0.6
K-6ϕ $C_6H_{4.35}K_{0.135}$	0.02_3	0.14	0.7
K-3ϕ $C_6H_{4.64}K_{0.273}$	0.02_0	0.11	1.1
K-3ϕ $C_6H_{4.67}K_{0.057}$	0.002	0.14	0.5
K-3ϕ $C_6H_{4.67}K_{0.02}$	0.008	0.14	1.6
Li-PPP $C_6H_{4.03}Li_{0.122}$	0.03_5	0.14	5.0-1.0

(a) Data from Reference 6 (inhomogeneously doped samples).

(b) Average values between 3 K - 100 K.

K-doped PPP, 6ϕ and 3ϕ, the spin concentration equals approximately 5-15% of the potassium concentration. However, as the concentration of dopant decreases in 3ϕ the spin concentration does not follow the dopant concentration proportionately, although the spin concentration does decrease. In a recent study of alkali-metal-doped PPP it was noted[6] that the unpaired spin concentrations were dependent on the alkali metal (Li - 30%; Na - 2.5%; K - 5%; Cs - 5%; Rb - 5%) while the spin concentration was found to be typically 10%

for all alkali-metal-doped deuterated PPP[6] (all heavily doped). Surprisingly, the T_m and T_1 values for K-PPP, K-3ϕ, and K-6ϕ are nearly temperature independent over the range from 2 K to 100 K (Figs 1-4). T_m is typically 140 ns and T_1 typically 500 to 1100 ns below 100 K. For K-PPP, $T \simeq 5T_m$ from 2 K to 100 K and $T_1 \simeq T_m$ at 300 K. For K-6ϕ, $T_1 \simeq 5T_m$ from 4 K to 100 K while at 300 K, $T_1 \simeq 2T_m$. On the other hand for heavily doped K-3ϕ, $T_1 \simeq 10T_m$ over the entire temperature range 20 to 300 K. As the concentration of K is decreased, $T_1 \simeq 3T_m$ over the entire temperature range for 0.057 moles of K per phenyl (Figs. 2,3), while for 0.02 moles of potassium per phenyl, $T_1 \simeq 10T_m$ from 20 K to 300 K.

Li-doped PPP has a somewhat similar temperature dependence below 100 K for T_1 and T_m (Figs. 2,3) to that observed for K-doped PPP. However, below 50 K, $T_1 \simeq 36T_m$; and T_1 is nearly an order of magnitude larger than that for K-PPP although the unpaired spin concentration is twice as large. At room temperature $T_1 \simeq 5T_m$.

DISCUSSION

Typically, the spin-lattice relaxation in metals is dominated by modulation of the spin-orbit coupling by thermal lattice vibrations. This gives rise to a temperature-dependent phonon contribution so that T_1 changes by several orders of magnitude between 2 and 100 K.[10,11] However, it has also been shown by Slichter and his co-workers[12-14] that if as much as 1 part in 10^7 impurities (large Z such as Au) exist in the metal under study, a temperature-independent relaxation mechanism can dominate whereby the conduction electrons interact with impurities. Relaxation by this mechanism comes mainly from the interaction of the conduction-electron spin with its orbital motion in the electric field of the impurity atom. This is a temperature-independent process which can be calculated by determining the spin-flip scattering cross section for conduction electrons in the electric field of the impurity.

According to the above mechanism, the linewidth and $1/T_1$ should depend linearly on the dopant concentration. Although our experimental data show temperature independence of T_1 and T_m, they also show no dopant concentration dependence. As a consequence, the above mechanism can not explain our results. In addition, later in this discussion, we shall show the observed unpaired spins are not carriers of conductivity; this also is incompatible with the above mechanism.

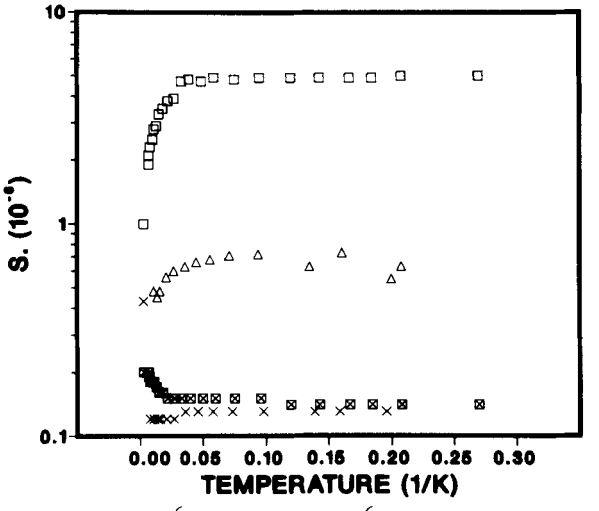

FIGURE 1. $T_1(10^{-6}s)$ and $T_m(10^{-6}s)$ versus reciprocal temperature (1/K) for K- and Li-doped PPP($C_6H_{4.20}K_{0.388}$ and $C_6H_{4.03}Li_{0.122}$). Triangle, K-doped T_1; cross, K-doped T_m; square, Li-doped T_1; square with cross, Li-doped T_m.

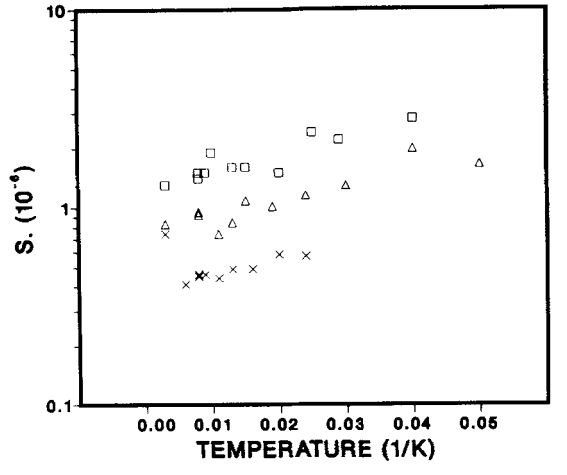

FIGURE 2. $T_1(10^{-6}s)$ versus reciprocal temperature (1/K) for K-doped $3\phi(C_6H_{4.64}K_{0.273})$, $3\phi(C_6H_{4.67}K_{0.057})$, and $3\phi(C_6H_{4.67}K_{0.02})$. Triangle, heavily-doped; cross, intermediately-doped; square, lightly-doped.

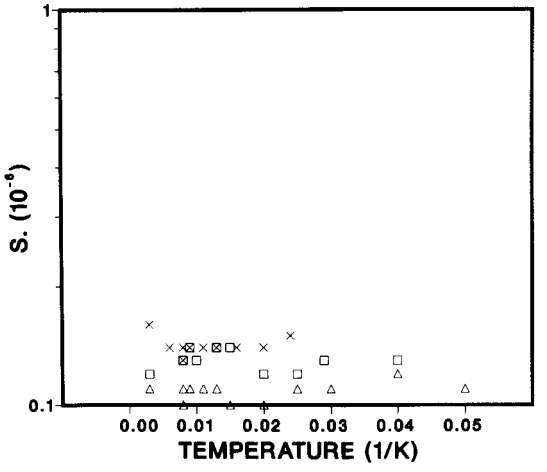

FIGURE 3. $T_m(10^{-6}s)$ versus reciprocal temperature (1/K) for K-doped $3\phi(C_6H_{4.64}K_{0.273})$, $3\phi(C_6H_{4.67}K_{0.057})$, and $3\phi(C_6H_{4.67}K_{0.02})$. Triangle, heavily-doped; cross, intermediately-doped; square, lightly-doped.

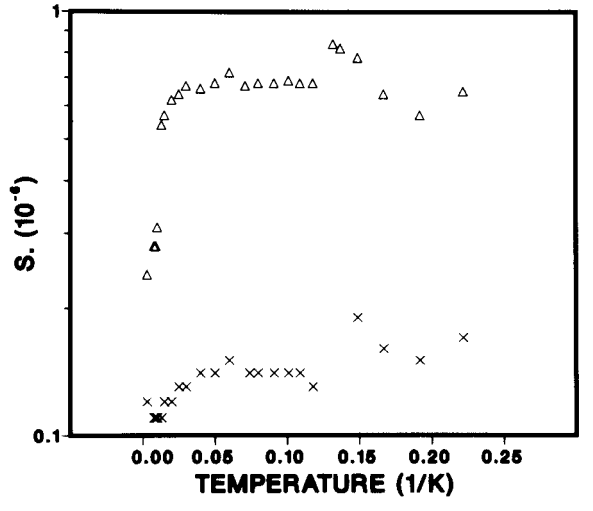

FIGURE 4. $T_1(10^{-6}s)$ and $T_m(10^{-6}s)$ versus reciprocal temperature (1/K) for K-doped $6\phi(C_6H_{4.35}K_{0.135})$. Triangle, T_1; cross, T_m.

In single crystals of graphite,[15] it has been observed that the single EPR line exhibits a Dysonian lineshape of a few Gauss' linewidth. The spin resonance is due to mobile charge carriers and shows a remarkably large g anisotropy; $g_{\perp}$ (300 K) = 2.0026 ± 0.0002, $g_{\parallel}$ (300 K) = 2.0495 ± 0.0002. The g-value anisotropy increases with decreasing temperature; $g_{\parallel}$ (77 K) = 2.127 and $g_{\perp}$ = 2.0029 ± 0.0002. Furthermore, the EPR intensity increases with temperature, in distinct contrast to the expected Curie-Law behavior. This observation can be rationalized by the fact that the numbers of carriers are proportional to T^2. In combination with a 1/T dependence from Boltzmann behavior, this gives rise to a linear dependence on temperature for the intensity.[15]

On the other hand, donor-doped graphite lamellar compounds exhibit[16] a much smaller g anisotropy than observed for graphite. Nevertheless, the EPR linewidth for stage I graphite shows a strong dependence on the intercalate: Li (≃2.5 G); K (11.4 Gauss) and Rb (190 Gauss) at 295 K. The observed g-value exhibits spin-orbit coupling to the metal: K- stage I (2.0016) and Rb-stage I (2.009).

In contrast, recent EPR studies of alkali-metal-doped PPP and deuterated PPP[6] indicate that the g-value is essentially independent of spin orbit coupling; g = 2.0027, 2.0030 and 2.0028 ± 0.0001 for Li-, Rb- and Cs-doped PPP. Furthermore, the linewidth at 300 K and at 10 K for donor-doped PPP does not increase with the spin orbit coupling of the alkali metal. Instead at 300 K, the linewidth increases in the order Li<Na<K<Cs<Rb, while at 10 K the linewidth increases in the order K<Li<Na<Cs<Rb. Furthermore, the linewidth decreases monotonically with decreasing temperature for Rb-, Cs- and K-doped PPP, and increases with decreasing temperature for Li- and Na-doped PPP. This absence of spin-orbit coupling strongly suggests that the observed spin resonance in donor-doped PPP is not that of charge carriers.

The identity of the radical system that gives rise to the narrow EPR lines in donor-doped PPP can be deduced by comparing the present results to an EPR study of single crystals of donor-doped biphenyl (Bp) grown from triglyme (Tg) or tetraglyme (Ttg).[17-20] An exchange average g-value was observed for each donor-doped biphenyl: for KBp.2Ttg (g = 2.00276);[17] for NaBp.2Tg (g = 2.00276);[18] for RbBp.2Ttg (g = 2.00275),[19] and was found to be equal to the Bp anion observed in solution. The linewidth for each system was angle-dependent and due to the electron dipole - electron dipole interaction between biphenyl anions separated from 9.65 to 7.6 Å apart. No electron density was observed on the metals. The calculated average linewidth

was similar to that observed for the donor-doped PPP samples. Typically, this is approximately 1.6 Gauss for KBp.2Ttg, 1.2 Gauss for NaBp.2Tg and 2.4 Gauss for RbBp.2Ttg. The EPR spectrum for each of these crystals was due to electron exchange narrowing of the biphenyl anion EPR signal by electron-electron exchange interactions between all neighboring biphenyl anions, with the main contribution from the biphenyl unit which occurred at less than 10 Å. The difference in linewidth was a direct function of the crystal packing arrangement with the biphenyl anions lying closest together (7.6 Å) in RbBp.2Ttg.

The similarity of the cw EPR spectrum for the donor-doped PPP samples with that of the K-, Na- and Rb- doped Bp suggests the EPR line in donor-doped PPP is due to electron-electron dipole interaction between neighboring anions or nonmobile radicals. The variation in linewidth with alkali metal suggests an inter- molecular dipole-dipole interaction between anions on neighboring chains of PPP.

It is necessary to justify the temperature independence of T_1 and T_m values if the EPR line is to be attributed to exchange narrowing between neighboring anions and not to charge carriers. It has been found[21] that the highly exchange-narrowed EPR line in DPPH exhibits a temperature-independent T_1 and T_2 value and that $T_1 = T_2 = 6.3 \times 10^{-8}$s. It was estimated that the exchange frequency equals 10 to 40 GHz. In addition, as the radical concentration decreases, T_1 becomes longer than T_2. Also, T_1 became temperature dependent. More recent studies[22] have shown that DPPH samples recrystallized from diffferent solvents were found to have different linewidths because the solvent molecules influence the free radical spacing and, thus, the exchange interaction. For broader lines, (2.8 G) $T_1=2T_2 = 5 \times 10^{-8}$s at the highest radical concentrations rather than $T_1=T_2=8 \times 10^{-8}$s for the narrowest line (0.8 G).

Thus, the small deviation from $T_1=T_m$ for K-doped PPP can be explained as due to a dependence of the spacing between radical anions. This is further substantiated by the fact that $T_1=36T_m$ for Li-PPP, a system where the distances between adjacent anions would be different due to the difference in size of Li and K. Furthermore, the ESE results support the assignment of the exchange narrowed EPR line in heavily donor-doped PPP as due to dipole-dipole exchange narrowing between neighboring anions. Captalizing on the similarity of the donor-doped PPP results to the biphenyl anions, a dipolar distance of 7.5 to 10 Å would be required in the PPP compounds. Such distances are quite reasonable for donor-donor distances expected in the PPP series studied here.

SUMMARY

No significant dependence of T_1 and T_2 on temperature was observed. The effect of the metal on linewidth is most likely due to the concomitant change in the donor-donor distances. It appears that the spins observed by EPR reside largely in the organic moities and not in the metals, as evidenced by a lack of g-value anisotropy. This failure to observe a spin-orbit coupling dependence on the g values and on the linewidths of the EPR signals from donor-doped PPP and its oligomers suggests that the EPR-observed free radicals are not the major carriers of conductivity. The results are more similar to those observed for donor-doped biphenyls where the EPR signals arise from anions firmly fixed in a crystal lattice. This similarity supports the view that in PPP and its oligomers the EPR signals arise from localized organic-like radicals. The observed linewidth probably arises by a dipole-dipole exchange narrowing between anions.

In summary, the ESE and EPR results given in this paper are consistent with the notion of bipolarons, i.e. pairs of correlated charged defects carrying no net spin, being the cause of the conductivity in doped PPP and its oligomers. A major point is that only 5% of the dopant appears to contribute to the EPR observable radical anions. Other possible mechanisms to explain the properties of these materials are being pursued.

ACKNOWLEDGMENTS

We wish to thank D. Ivory, L. Shacklette, R. Baughman, G. Miller, and J. Hyde for numerous helpful discussions and the Allied Corp. for the PPP and 6ϕ samples. This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contracts W-31-109-ENG-38 and DE-As05-76ER04062.

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