

## Triplet Energies of $\pi$ -Conjugated Polymers

A. P. Monkman,<sup>1</sup> H. D. Burrows,<sup>2</sup> L. J. Hartwell,<sup>1</sup> L. E. Horsburgh,<sup>1</sup> I. Hamblett,<sup>3</sup> and S. Navaratnam<sup>3</sup>

<sup>1</sup>*Department of Physics, University of Durham, Durham, United Kingdom*

<sup>2</sup>*Department of Chemistry, University of Coimbra, 3049 Coimbra, Portugal*

<sup>3</sup>*Paterson Institute for Cancer Research, Christie Hospital, Manchester, United Kingdom*

(Received 4 April 2000)

Using pulse radiolysis and triplet energy transfer has enabled us to measure the triplet energies in a broad range of different  $\pi$ -conjugated polymers. In all cases we find that the  $1^3B_u$  is of order 0.6 to 1 eV below the  $1^1B_u$ , indicative of localized triplet states with strong electron-electron correlation. We also observe that the  $1^1A_g-1^3B_u$  gap decreases linearly as the  $1^1A_g-1^1B_u$  gap decreases even though polymers with very different structure have been studied. This surprising result suggests that polymers with singlet gap  $<1.3$  eV will have a triplet ground state.

DOI: 10.1103/PhysRevLett.86.1358

PACS numbers: 78.66.Qn, 71.20.Rv, 71.35.-y

Luminescent conjugated polymers are a new technologically important class of materials which will be used in light emitting display devices for the next generation of information technology based consumer products [1,2]. Their photophysical properties are complex, with many different excited states and other transient species having been observed over various time domains [3,4]. However, the nature and photophysics of triplet states in these materials is not well characterized. This is an important omission since triplet states are generally believed to be the dominant species formed on charge recombination which yields electroluminescence, the basis for both polymer light emitting diodes and potential electrically pumped polymeric lasers. This is because charge recombination spin statistics dictate that only ca. one singlet exciton is formed for every three triplet excited states (excitons) [5]. Thus, to be able to produce better materials, more efficient devices, and gain a deeper insight into these polymers, the basic characterization of their triplet states is vital. Further, by comparing the relative energies of the singlet and triplet "gaps" an estimate of the strength of electron-electron correlation in these polymers can be made. In the case of strong correlation, the exciton model would be favored over a band picture as the description of these materials. However, such measurements are not trivial, due, in general, to the very low intersystem crossing rates in these materials [6–8] and their low phosphorescence quantum yields [9]. Hence via direct optical excitation it has not generally been possible to measure triplet energies [10]. Therefore, we have turned to an alternative route to produce triplet states in these polymers, one in which both the kinetics of the triplets and more importantly their energies can be measured. We recently reported on the use of pulse radiolysis to measure the triplet energy in poly[2-methoxy,5-(2'-(ethylhexoxy)-*p*-phenylenevinylene)] (MEHPPV) [7]. We have also demonstrated that charged states, again generated by this method, have very different lifetimes and spectral signatures from the triplet states [11]. We now report on triplet state measurements on a range of the most widely used luminescent and conductive polymers in current dis-

play technologies; see Fig. 1. In general we find, as in acenes, the energy of the first triplet state,  $1^3B_u$ , to be typically  $\frac{2}{3}$  that of the first singlet  $1^1B_u$  excited state, indicative of strong electron-electron correlation.

Since the classic work of Terenin and Ermolaev [12], triplet-triplet energy transfer has become one of the most important methods of specifically generating triplet states of organic molecules. Coupling this with pulse radiolysis of solutes in organic solvents provides an excellent technique for the selective creation and study of both excited states and charged species [13–15]. An intense, 10–100 ns pulse of electrons (accelerated to 10 MeV) from a linear accelerator irradiates the sample. The radiation chemistry of solutions is dominated by the most prevalent species in solution, the solvent [13]. The primary excitation process involves ionization which in aromatic solvents such as benzene (Bz) is rapidly followed by charge recombination ( $<1$  ns), leading to excited triplet and singlet state generation in the statistical ratio 3:1 (in the benzene). By using appropriate energy acceptors (A), such as biphenyl, having lower triplet energies than benzene, short-lived singlet excited states and high  $S_1 \rightarrow T_1$  intersystem crossing efficiencies, the excited triplet state of this acceptor can be selectively produced and subsequently transfer the triplet energy to the molecule under investigation (S), i.e., our polymers, subject to the kinetically demanded concentration ratio  $[Bz] \gg [A] \gg [S]$  [16]. This concentration gradient, combined with diffusion controlled collisional triplet energy transfer (in solution) ensures that effectively only triplet energy is transferred down to the molecule under investigation. Transient induced optical absorption spectra are used to monitor triplet state grow-in and decay and ground state bleaching. We have on the order of 20 appropriate acceptors/donors available to us [17] with well characterized  $T_1$  energies  $E_{TA}$ , each within 0.1 to 0.2 eV of the next. A series of measurements are made to determine which acceptor transfers triplet energy to the polymer. When  $E_{TA} < E_{TS}$  no induced triplet absorption is observed since no triplet transfer to our polymer is

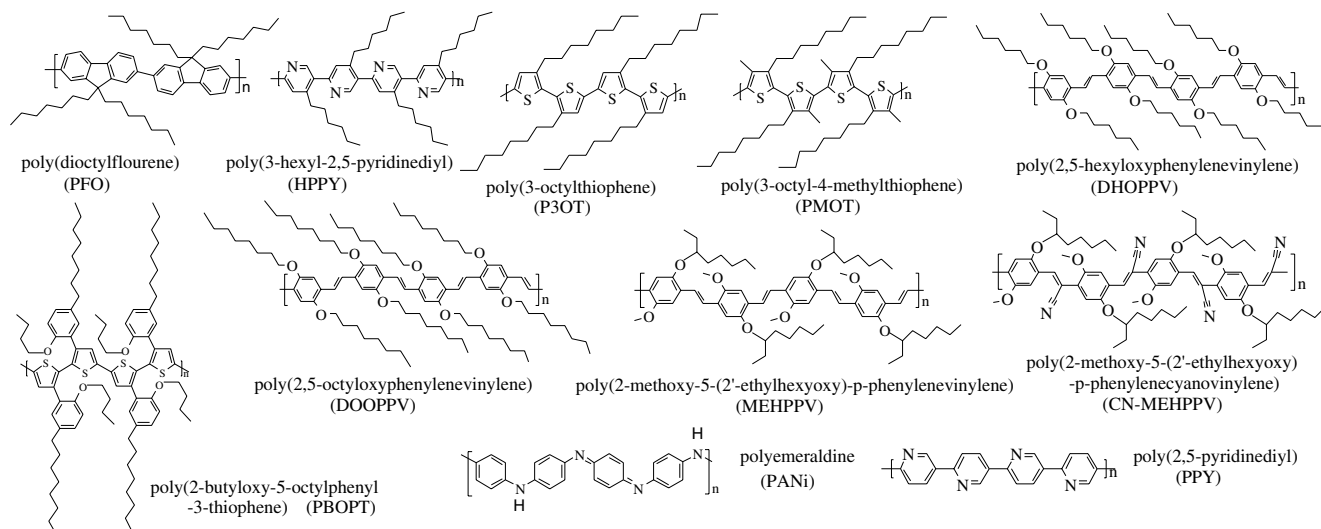


FIG. 1. Schematic pictures of the chain structures of the polymers used in this work and the acronyms used in Table I and the text.

possible, thus enabling an upper limit to be placed on the triplet energy of the polymer. For the range of acceptors available to us we can estimate the triplet energy of the polymer to within  $\pm 0.05$  to 0.1 eV in most cases.

To verify the validity of this technique, a comparison to a direct optical measurement of a conjugated polymer triplet state is needed. Recently Romanovskii *et al.* were able to observe weak phosphorescence from the ladder polyparaphenylene, MeLPPP [9]. At 77 K in the solid

state they determine a triplet energy of  $16\,500\text{ cm}^{-1}$ , 2.05 eV. We have now made a radiolysis experiment, in benzene solution at room temperature, on MeLPPP yielding a value of  $2.15 \pm 0.1$  eV. Given the small difference between absorption and emission in solution compared to solid state in MeLPPP this agreement is very satisfactory and now gives strong support for the radiolysis methodology. More details on these measurements are reported in a separate publication [18].

TABLE I. Photophysical data obtained by pulse radiolysis for triplet states in various conjugated polymers;  $\Delta E_{ST}$  is the energy difference between the  $1^1\text{Bu}$  and the  $1^3\text{Bu}$  states.

Polymer	$S_0$ - $S_1$ energy (eV)		PL	$T_1$ - $S_0$ (eV)	$T_1$ - $T_n$ (eV)	$\tau_T$ ( $\mu\text{s}^a$ )	$\Delta E_{ST}$ (eV)	
	Maximum <sup>b</sup>	Onset <sup>c</sup>					Maximum <sup>b</sup>	Onset <sup>c</sup>
PMOT	3.77 (329)	3.22 (385)	2.64 (469)	2.20	1.85 (670)	62	1.57	1.02
P3OT	2.83 (438)	2.42 (512)	2.21 (562)	1.65	1.50 (825)	21	1.03	0.62
PBOPT	2.52 (492)	2.18 (570)	2.17 (572)	1.60	1.38 (900)	57	0.92	0.58
MEHPPV	2.48 (500)	2.23 (556)	2.25 (550)	1.30	1.50 (830)	92	1.18	0.93
PFO	3.22 (385)	3.01 (412)	3.00 (413)	2.30	1.65 (750)	108	0.92	0.71
DOOPPV	2.59 (478)	2.23 (556)	2.28 (544)	1.50	1.55 (800)	134	1.09	0.73
DHOPPV	2.58 (480)	2.13 (581)	2.30 (538)	1.50	1.62 (765)	176	1.08	0.63
PPY	3.35 (370)	3.10 (400)	3.26 (380)	2.40	2.10 (590)	98	0.95	0.70
HPPY	3.90 (318)	3.50 (344)	2.82 (440)	2.50	2.10 (590)	70	1.40	1.00
CN-MEHPPV	2.72 (456)	2.35 (527)	2.28 (544)					
PANi <sup>d</sup>	2.00	1.77 (700)	N/A	<0.9	1.55 (800)	ca. $2.4 \geq 2000$	<1.1	<0.9

<sup>a</sup>Triplet state lifetime in benzene solution; <sup>b</sup>from maximum of absorption band; <sup>c</sup>from onset of absorption band; <sup>d</sup>measured in 80% benzene/20% *N*-methylpyrrolidone.

The results of our triplet energy measurements are summarized in Table I. Triplet lifetimes in benzene solution are also given. It can be noted that the lifetimes for the polythiophenes are markedly shorter than those of the other polymers. This is in agreement with observations on triplet states of oligothiophenes [19] and time resolved induced absorption measurements on P3OT [20] and is consistent with significant spin orbit coupling involving the sulfur atom in each repeat unit increasing intersystem crossing. For CN-MEHPPV we find that a metastable transient species (either an isomer or degradation product) appeared to have formed via the triplet state. Only an upper limit of  $<2.6$  eV can be made for the triplet energy in this case. All of the polymer triplet states except that of polyaniline emeraldine base (PANi) were quenched by oxygen. Thus, for PANi it was possible only to estimate an upper limit on the  $T_1$  energy.

To determine if there are any general trends between singlet and triplet energies and polymer structure, in Fig. 2 we plot the  $1^1A_g-1^3B_u$  ( $S_0-T_1$ ) energy gap against the  $1^1A_g-1^1B_u$  ( $S_0-S_1$ ) separation, as measured from the maximum of the singlet absorption band. A very striking linear correlation between the singlet and triplet energies is found for the very different polymers studied here. This is a very unexpected result. We note that a similar trend can be found with the acenes [21]. As a first approximation, for the conjugated polymers a least squares fit to the data yields

$$T_1 = (1.13S_1 - 1.43) \pm 0.25 \text{ eV}.$$

Several important points can be deduced from this finding. The triplet gap decreases along with the reduction in singlet gap. By extrapolation it is possible to predict that a polymer will have a triplet ground state when the singlet energy gap is ca.  $1.3 \pm 0.25$  eV. For comparison, with polyacenes it is suggested that the first member with a triplet ground state will be nonacene [21]. From literature data, we estimate an energy for its lowest singlet state to be ca. 1.3–1.5 eV. The corresponding energies for the heterocyclic polyacenes may be even lower [22]. Thus the conjugated polymers would seem to behave in an identical fashion to the polyacenes and by comparison the conjugation length in polymers must be ca. nine repeat units.

The reduction of the singlet gap, i.e., the decrease in singlet exciton energy, as conjugation length increases is generally accepted to imply that increased conjugation length delocalizes excitations on the polymer chain. This is borne out in many experiments on oligomeric compounds; for example, see Refs. [23] and [24], where it is found that the  $\Delta E_S(L) = \Delta E_S(\infty) + C_S/L$ , where  $\Delta E_S$  is the singlet gap,  $L$  is the chain length, and  $C_S$  is a constant [23]. As the triplet states are essentially made up of the same orbitals as the singlets, a similar relationship should hold for the triplet states; i.e.,  $\Delta E_T(L) = \Delta E_T(\infty) + C_T/L$ . For the case where  $C_T < C_S$  the singlet-triplet gap will decrease as  $L$  increases. In our experiments, each backbone is different; thus the values of the constants in these relation-

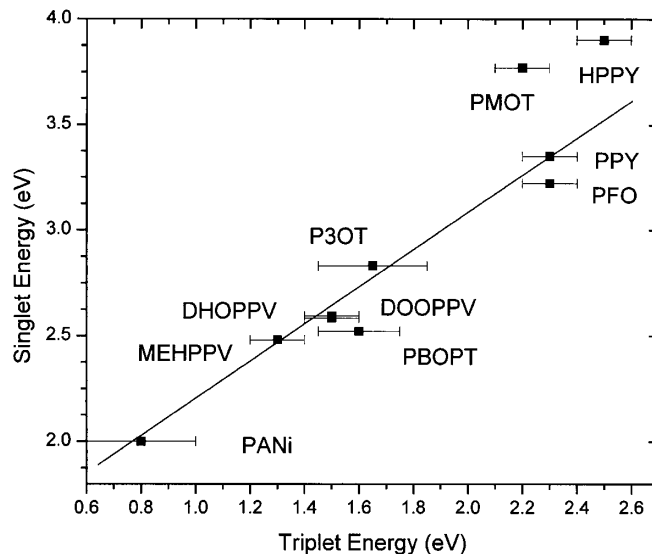


FIG. 2. Plot of triplet energy gap against singlet energy gap for different polymers. Polymer acronyms given in Fig. 1. The line is a guide to the eye.

ships will be different. However, the general trend that we observe for this broad range of conjugated polymers is that the triplet gap decreases as the singlet gap decreases, i.e., delocalization increases, implying that  $C_T < C_S$  is true for conjugated polymers in general. Although we have studied only three polythiophene derivatives, they do fit on a good straight line; in these cases the backbone is the same and only the conjugation length is different, caused by torsional distortion from the sidegroups [25]. We are in the near future going to measure more of this family of polymers to verify these initial trends. The physical consequence of  $C_T < C_S$  is that the triplet states must be more tightly bound than the singlet states, i.e., more localized, but their degree of localization is affected by the chain backbone. This general conclusion is in agreement with the observation of vibronic structure on the triplet-triplet absorption band, indicating a structurally relaxed triplet state [7,17]. Theoretical predictions [26–28], work on model systems [9,10], and the observation of long-lived phosphorescence in a ladder poly(phenylene) [29] are also consistent with localized triplet states. In addition, it is difficult to explain the relatively low triplet mobility on these polymer chains, or the observation of delayed fluorescence following triplet-triplet annihilation [18], unless they are more tightly bound than the corresponding singlet states.

The large electron-electron correlation seen in all these polymers implies that the on site repulsion energy  $U$  is large. Abe *et al.* have shown that for the  $1^3B_u$  to be appreciably lower than the  $1^1B_u$ , the ratio  $U/V > 2$ , where  $V$  is the long range Coulomb interaction [30]. In the case where  $U$  is large, the triplet electrons can be in the same molecular orbital with a minimum of repulsion. This again is consistent with localized triplet states. In the solid state this scenario would strongly support the exciton picture over the band model. As we find the same triplet energy

in solution as is found in solid state for MeLPPP and also find very little difference between triplet-triplet absorption energies in solution and solid state, we assume that there is little change in the strong electron-electron correlation when weak interchain interactions are introduced in the solid state.

To conclude, we have now measured the triplet energies of a wide range of conjugated polymers, in the main those predominant in the areas of light emitting devices. Comparing these energies with the corresponding singlet energy it can be seen that in all cases the triplet state is at a much lower energy than the singlet indicative of a large electron-electron correlation energy. A general trend is observed between the singlet and triplet energy gaps. For all the various types of conjugated polymers studied here there exists a linear relationship between singlet and triplet gaps. The confirmation that triplet energies determined by our method yield very similar values to those found by phosphorescence in the solid state allows the triplet energies given here to be used as a good guide to the triplet energies in the solid state as well as the isolated chain case. Full understanding of electron correlation in the excited states of these conjugated polymers requires detailed quantum mechanical treatment, but the experimental data presented on triplet energies represent both a challenge to theoreticians and a good starting point for high level calculations. One very obvious initial prediction from this work is that a polymer with a singlet gap below ca. 1.3 eV should have a triplet ground state.

We acknowledge the EPSRC (GR/M86040), PRAXIS XXI (Project No. 2/2.1/QUI/411/94), and the British Council/CRUP (Project No. B-9/97) for financial support. We thank and acknowledge for their very kind supply of materials Covion (MEH-PPV), Professor M. Andersson (polythiophenes), Professor U. Scherf (PFO), M. de Long (DOO and DHO PPV), and Professor A. Holmes (CN-MEHPPV). We also thank the Paterson Institute for Cancer Research Free Radical Research Facility (Manchester, UK) for access to the pulse radiolysis spectrometer, Dr. Donald Allan for all of his help and Scottish history lessons, and Professor H. Bässler for enlightening discussions.

- 
- [1] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. dos Santos, J. L. Brédas, M. Lögdlund, and W. R. Salaneck, *Nature* (London) **397**, 121 (1999).  
 [2] R. J. Visser, *Philips J. Res.* **51**, 467 (1998).  
 [3] N. T. Harrison, G. R. Hayes, R. T. Phillips, and R. H. Friend, *Phys. Rev. Lett.* **77**, 1881 (1996).  
 [4] S. V. Frolov, W. Gellermann, M. Ozaki, W. Gellermann, K. Yoshino, and Z. V. Vardeny, *Phys. Rev. Lett.* **78**, 729 (1997).

- [5] M. A. Baldo, D. F. O'Brien, M. E. Thompson, and S. R. Forrest, *Phys. Rev. B* **60**, 14 422 (1999).  
 [6] R. D. Scurlock, B. Wang, P. R. Ogilby, J. R. Sheats, and R. L. Clough, *J. Am. Chem. Soc.* **117**, 10 194 (1995).  
 [7] A. P. Monkman, H. D. Burrows, M. da G. Miguel, I. Hamblett, and S. Navaratnam, *Chem. Phys. Lett.* **307**, 303 (1999).  
 [8] J. Seixas de Melo, C. S. Soare, A. P. Monkman, H. Burrows, and L. G. Arnaut (to be published).  
 [9] Yu. V Romanovskii, A. Gerhard, B. Schweitzer, U. Scherf, R. I. Personov, and H. Bässler, *Phys. Rev. Lett.* **84**, 1027 (2000).  
 [10] K. A. Walters, K. D. Ley, and K. S. Shanze, *Chem. Commun. No. 10*, 1115 (1998).  
 [11] H. D. Burrows, M. da G. Miguel, A. P. Monkman, L. E. Horsburgh, I. Hamblett, and S. Navaratnam, *J. Chem. Phys.* **112**, 3082 (2000).  
 [12] A. N. Terenin and V. Ermolaev, *Trans. Faraday Soc.* **52**, 1042 (1956), and references therein.  
 [13] J. H. Baxendale and M. A. J. Rodgers, *Chem. Soc. Rev.* **7**, 235 (1978).  
 [14] A. J. Swallow, in *Radiation Chemistry, Principles and Applications*, edited by Farhataziz and M. A. J. Rodgers (VCH, New York, 1987).  
 [15] J. H. Baxendale and M. Fiti, *J. Chem. Soc. Faraday Trans. 2* **68**, 218 (1972).  
 [16] E. J. Land, *Proc. R. Soc. London A* **305**, 457 (1968); R. Bensasson and E. J. Land, *Trans. Faraday Soc.* **67**, 1904 (1971).  
 [17] A. P. Monkman, H. D. Burrows, L. E. Horsburgh, L. J. Hartwell, M. da G. Miguel, I. Hamblett, and S. Navaratnam, *Proc. SPIE Int. Soc. Opt. Eng.* **3797**, 109 (1999).  
 [18] A. P. Monkman, H. D. Burrows, I. Hamblett, S. Navaratnam, U. Scherf, and C. Schmitt, *Chem. Phys. Lett.* **327**, 111–116 (2000).  
 [19] J. Seixas de Melo, L. M. Silva, L. G. Arnaut, and R. S. Becker, *J. Chem. Phys.* **111**, 5427 (1999).  
 [20] B. Kraabel, D. Moses, and A. J. Heeger, *J. Chem. Phys.* **103**, 5102 (1995).  
 [21] H. Angliker, E. Rommel, and J. Wirz, *Chem. Phys. Lett.* **87**, 208 (1982).  
 [22] Th. Starssner, A. Weitz, J. Rose, F. Wudl, and K. N. Houk, *Chem. Phys. Lett.* **321**, 459 (2000).  
 [23] J. Grimme, M. Kreyenschmidt, K. Müllen, and U. Scherf, *Adv. Mater.* **7**, 292 (1995).  
 [24] H. S. Woo, O. Lhost, S. C. Grahem, D. D. C. Bradley, R. H. Friend, C. Quattrocchi, J.-L. Brédas, R. Schenk, and K. Müllen, *Synth. Met.* **59**, 13 (1993).  
 [25] M. R. Andersson, O. Thomas, W. Mammo, M. Svensson, M. Theander, and O. Inganäs, *J. Mater. Chem.* **9**, 1933 (1999).  
 [26] D. Beljonne, Z. Shuai, R. H. Friend, and J.-L. Brédas, *J. Chem. Phys.* **102**, 2042 (1995).  
 [27] M. Chandross and S. Mazumdar, *Phys. Rev. B* **55**, 1497 (1997).  
 [28] D. A. dos Santos, D. Beljonne, J. Cornil, and J. L. Brédas, *Chem. Phys.* **227**, 1 (1998).  
 [29] Yu. V. Romanovskii and H. Bässler, *Chem. Phys. Lett.* **326**, 51 (2000).  
 [30] S. Abe, J. Lu, and W. P. Su, *Phys. Rev. B* **45**, 8264 (1992).