Synthesis and Optoelectronic Properties of Aromatic Oxadiazole Polymers

Xiao-Chang Li,[a] Andrew B. Holmes,*[b] Arno Kraft,[a] Stephen C. Moratti,[b] George C. W. Spencer,[a] Franco Cacialli,[c] Johannes Grüner[c] and Richard H. Friend[c]

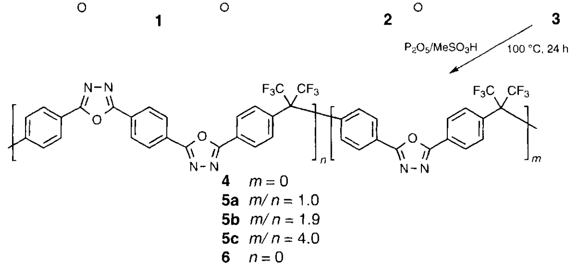
[a] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*
[b] *Melville Laboratory for Polymer Synthesis, University of Cambridge, Pembroke Street, Cambridge, UK CB2 3RA*
[c] *Department of Physics, University of Cambridge, Madingley Road, Cambridge, UK CB3 0HE*

A one-pot polycondensation of 4,4′-(hexafluoroisopropylidene)bis(benzoic acid) **1** with terephthalic dihydrazide **2** and/or hydrazine sulfate **3** affords aromatic oxadiazole polymers **4**, **5** and **6**, respectively, the optical and electrochemical properties of which have been investigated for applications as charge transporting layers in electroluminescent devices.

Aromatic oxadiazole polymers have been widely studied as thermally stable and high modular high strength materials.[1–5] They can also be used as membrane separation and hydrolytically stable materials by proper molecular design.[6–8] Little work on their optical and electronic properties has been published, although poly(phenylene-1,3,4-oxadiazoles) have recently been studied as n-doped polymers,[9] and intrinsic conducting polymers after carbonisation processes.[10] Aromatic oxadiazole compounds have been used as efficient scintillators and electron transporting/injection materials in organic light emitting diodes (LEDs) due to their strong photoluminescence and relatively high electron affinity.[11–15] For use as an electron transporting layer in LEDs, polymers covalently bonded with aromatic oxadiazole rings would be better than those blended with aromatic oxadiazoles.[16] We[17] and others[18] have shown that the incorporation of oxadiazole chromophores in the side chain of polymethacrylate polymers or copolymers can improve polymer LEDs performance. During the course of the preparation of this manuscript, the known poly(phenylene-1,3,4-oxadiazole-phenylene-hexafluoropropylene) **6**[19] was reported to be effective as an electron-transporting material in polymer LEDs.[20] Here we report a broader approach to obtain processible main-chain aromatic oxadiazole (co)polymers with tunable properties. The synthesis and optical and electrochemical redox properties of such materials are presented.

Aromatic oxadiazole polymers **4** and **6** have been synthesised by a one-pot reaction of the diacid **1** with the dicarboxylic hydrazide **2** and/or hydrazine sulphate **3** respectively at 100 °C in the presence of P_2O_5–$MeSO_3H$ which serves both as solvent and cyclodehydrating agent. In order to obtain soluble polymers, the flexible hexafluoropropylidene spacer has been introduced into the polymers. This was selected for its flexibility and weak intermolecular forces (Scheme 1). The hexafluoropropylidene linkage was also expected to hinder crystallinity and limit conjugation in addition to enhancing electron affinity of the polymers.

Polymer **4** is a colourless powder with the onset of UV–VIS absorption at λ = 383 nm (HOMO–LUMO gap of 3.24 eV) and exhibits bright blue fluorescence under UV irradiation. The absorption and photoluminescence emission spectra of **4** are shown in Fig. 1. Measurement of the photoluminescence efficiency using an integrating sphere[21] showed values close to 50% for thin solid films of **4**. The fibre-like polymer **6** fluoresced in the purple region under UV irradiation (HOMO–LUMO gap 3.73 eV). The advantage of compound **6** over compound **4** is its good solubility in chlorinated solvents. In contrast, polymer **4** is not soluble in common organic solvents, but is soluble in strong acids such as trifluoroacetic acid. In order to adjust the properties, copolymers with different ratios of compounds **4** and **6** have been synthesised. As shown in Table 1, the properties of the copolymers **5** can be tailored according to the ratio of **4** to **6**. With an increasing fraction of the repeat unit **6**, the copolymer becomes more soluble in chloroform (**5b** is partially soluble in chloroform and **5c** is completely soluble in chloroform). The HOMO–LUMO gap and UV absorption maxima of the polymers can also be changed according to the ratio of the two repeat units.



Scheme 1 The synthesis of the aromatic oxadiazole polymers **4**, **5** and **6**

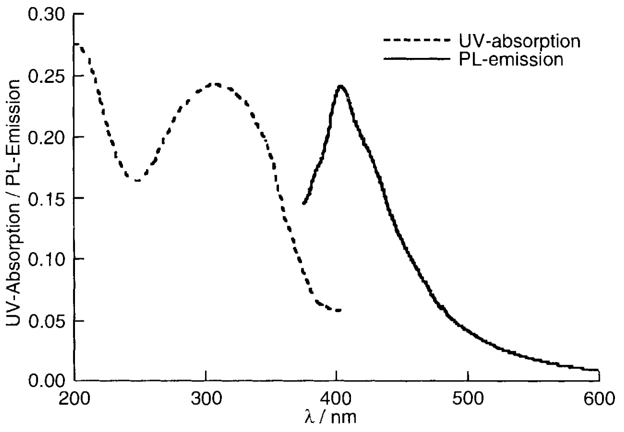


Fig. 1 UV–VIS absorption and photoluminescence emission spectra of the film of polymer **4**

Table 1 Properties of aromatic oxadiazole polymers **4–6**

Polymer	Solubility[a]	λ_{max} (film)/nm	E_g/eV[b]	E_{pc}/E_{pa}/V[c]
4	$CHCl_3$ (n) CF_3CO_2H (s)	306	3.24	−1.92/−1.90, −2.20/−2.18
5a	$CHCl_3$ (n) CF_3CO_2H (s)	302	3.43	−1.92/−1.89, −2.27/−2.16
5b	$CHCl_3$ (p) CF_3CO_2H (s)	294	3.44	−1.98/−1.92, −2.28/−2.16
5c	$CHCl_3$ (s)	290	3.47	−2.00/−1.95, −2.29/−2.15
6	$CHCl_3$ (s)	286	3.73	−2.05/−2.02, −2.29/−2.15

[a] n = not soluble; s = soluble; p = partially soluble. [b] HOMO–LUMO gap measured according to the onset of UV-absorption. [c] Peak potential of anodic (E_{pa}) and cathodic (E_{pc}) peak respectively (*vs.* 0.1 mol dm^{-3} Ag/Ag$^+$) measured between neutral and reduced states with a film on a platinum disc electrode in acetonitrile solution containing $(Bu)_4NClO_4$ (0.1 mol dm^{-3}).

The two homopolymers **4**, **6** and their copolymers **5a–c** are all colourless. Transparent thin films can be easily obtained by a casting technique. All the polymers were found to be very stable, even in strong acid such as concentrated sulfuric acid, and did not melt below 220 °C. The molar masses of **5c** and **6** have been measured by gel permeation chromatography (GPC) analysis using poly(styrene) as a standard (**5c** $M_w:M_n$ = 177 000:41 000; **6** 143 000:12 000).†

In order to understand the potential use of these materials for charge injection and electron-transporting/hole-blocking in LEDs, the polymer films have been studied by CV. This was accomplished in a typical three-electrode cell with a polymer film on a working platinum electrode. It was found that all the polymers are oxidised with difficulty even at high potential (*ca.* 1.6 V *vs* 0.1 mol dm^{-3} Ag/Ag$^+$) as compared with other conjugated polymers (0.6–1.0 V).[22] The result suggests that this series of polymers has a low LUMO and excellent hole-blocking properties.

On the other hand, all the polymers were found to be reducible as shown in Fig. 2. From the half-wave reduction peak position (cathodic potential), the polymer **4** is estimated to be more easily n-doped (or reduced) than polymer **6**. It is interesting to note that there are two apparent cathodic half-wave reduction potentials for polymers **4** and **5a–c** around −1.9 to −2.0 V (*E*pc), and they are reversed on the oxidation sweep as summarised in Table 1. For polymer **6**, there is still a weak but detectable cathodic (and corresponding anodic) peak at −2.29 V (and −2.15 V). This two step reduction process has rarely been observed in well conjugated polymers such as poly(cyanoterephthalylidene) (CN-PPV),[22] probably because of the well π-delocalised polymer chain. In conjugated heteroaromatic alternating copolymers, a main peak with a shoulder in the cyclic voltammogram has been observed[9,23] which has been assigned to the n-doping of two different heterocyclic rings. An alternative possibility is that radical anions are formed in the first step, and then reduced in a second reduction to a dianion.

For a further evaluation of the charge injection/transporting properties of the polymers, the polyaromatic oxadiazoles have been tested as electron transporting layer (between an emissive polymer and cathode) in LEDs. It was found that the use of polyaromatic oxadiazole polymer can assist in achieving light emission using stable cathode metals such as aluminium.

We thank the EPSRC and the European Commission (ESPRIT project No. 8013 'LEDFOS'; Brite-EURAM contract 'POLYLED', BRE2-CT93-0592) for financial support. We thank the EPSRC Swansea Mass Spectrometry Service for mass spectra.

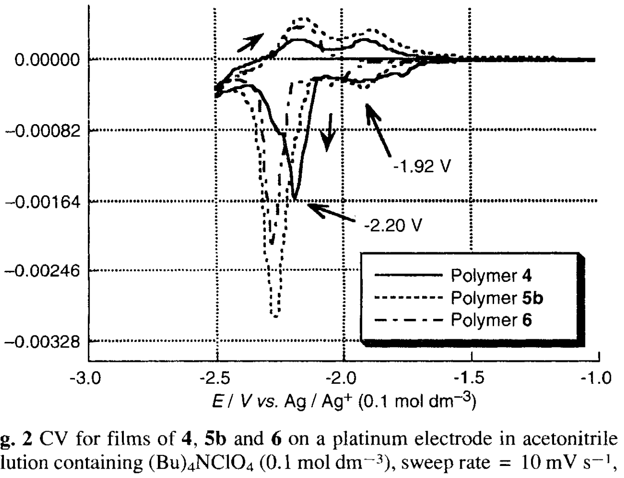


Fig. 2 CV for films of **4**, **5b** and **6** on a platinum electrode in acetonitrile solution containing $(Bu)_4NClO_4$ (0.1 mol dm^{-3}), sweep rate = 10 mV s^{-1}, at 20 °C

Received, 24th May 1995; Com. 5/03332B

Footnote

† All new compounds have been characterised by UV–VIS absorption, FTIR, NMR and microanalysis. Data for polymer **6** (*J* values in Hz; multiplicity of carbon resonances determined by APT experiment – e = methylene and quaternary, o = methine and methyl): δ_H (400 MHz, $CDCl_3$) 7.60 (4 H, d, *J* 8), 8.18 (4 H, d, *J* 8); δ_C (100 MHz, $CDCl_3$) 122.3 (e), 124.8 (e), 125.3 (e), 127.1 (o), 131.0 (o), 136.5 (e); ν_{max} (KBr)/cm^{-1} 1618, 1585, 1551, 1499, 1420, 1256, 1210, 1175, 1140, 1071, 971, 928, 840 and 723.

References

1 A. H. Frazer and I. M. Sarasohn, *J. Polym. Sci.*, 1966, **A-4**, 1649.
2 I. K. Varma and C. K. Greetha, *J. Appl. Polym. Sci.*, 1978, **22**, 411.
3 M. Ueda and M. Oda, *Polym. J.*, 1989, **21**, 193.
4 H. C. Bach, F. Dobinson, K. R. Lea and J. H. Saunders, *J. Appl. Polym. Sci.*, 1979, **23**, 2125.
5 C. Kummerloewe, H. W. Kammer, M. Malincomico and E. Martuscelli, *Polymer*, 1991, **32**, 2505.
6 E. R. Hensema, J. P. Boom, M. H. V. Mulder and C. A. Smolders, *J. Polym. Sci., Polym. Chem.*, 1994, **32**, 513.
7 B. Grebben, M. H. V. Mulder and C. A. Smolders, *J. Membrane Sci.*, 1989, **46**, 29.
8 J. W. Fitch, P. E. Cossidy, W. J. Weikel, T. M. Lewis, T. Trial, L. Burgess, J. L. March, D. E. Glowe and G. C. Rolls, *Polymer*, 1993, **34**, 4796.
9 S. Janietz, B. Schulz, M. Törrönen and G. Sundholm, *Eur. Polym. J.*, 1993, **29**, 545.
10 Y. B. Roh, H. Araki, K. Yoshino, M. Tokase and T. Banjyo, *Jpn. J. Appl. Phys.*, 1994, **33**, 1146.
11 F. N. Hayes, B. S. Rogers and D. G. Ott, *J. Am. Chem. Soc.*, 1955, **77**, 1850.
12 C. Adachi, S. Tokito, T. Tsutsui and S. Saito, *Jpn. J. Appl. Phys.*, 1988, **27**, L713.
13 Y. Hamada, C. Adachi, T. Tsutsui and S. Saito, *Jpn. J. Appl. Phys.*, 1992, **31**, 1812.
14 S. Lunak, Jr., M. Nepras, A. Kurfurst and J. Kuthan, *J. Chem. Phys.*, 1993, **170**, 67.
15 K. Naito and A. Miura, *J. Phys. Chem.*, 1993, **97**, 6240.
16 P. L. Burn, A. B. Holmes, A. Kraft, A. R. Brown, D. D. C. Bradley and R. H. Friend, in *Electrical, Optical, and Magnetic Properties of Organic Solid State Materials (MRS Symposium N, Fall Meeting Boston 1991)*, ed. L. Y. Chiang, A. F. Garito and D. J. Sandman, *Mater. Res. Soc. Symp. Proc.*, 1992, **247**, 647; A. R. Brown, D. D. C. Bradley, J. H. Burroughes, R. H. Friend, N. C. Greenham, P. L. Burn, A. B. Holmes and A. Kraft, *Appl. Phys. Lett.*, 1992, **61**, 2793.
17 X.-C. Li, F. Cacialli, M. Giles, J. Grüner, R. H. Friend, A. B. Holmes and S. C. Moratti, *Proc. Am. Chem. Soc. Div. Polym. Mater., Sci. Eng.*, 1995, **72**, 463.
18 M. Strukelj, F. Papadimitrakopoulos, T. M. Miller and L. J. Rothberg, *Science*, 1995, **267**, 1969.
19 B. R. Livshits, S. V. Vinogradova, I. L. Knunyunts, G. L. Berestneva and T. K. L. Dymoshits, *Vysokomol. Soyed. Ser. A*, 1973, **15**, 961; *Chem. Abstr.* 1973, **79**, 105603h; E. R. Hensema, M. E. R. Sena, M. H. V. Mulder and C. A. Smolders, *J. Polym. Sci., Polym. Chem.*, 1994, **32**, 513.
20 Y. Yang and Q. Pei, *J. Appl. Phys.*, 1995, **77**, 4807; Q. Pei and Y. Yang, *Adv. Mater.*, 1995, **7**, 559.
21 N. C. Greenham, R. H. Friend and D. D. C. Bradley, *Adv. Mater.*, 1994, **6**, 491.
22 S. C. Moratti, D. D. C. Bradley, R. Cervini, R. H. Friend, N. C. Greenham and A. B. Holmes, in *Advanced Materials for Information Technology* ed. S. Estemad, SPIE Proceedings, 1994, **2144**, 108.
23 T. Kanbara, Y. Miyazaki and T. Yamamoto, *J. Polym. Sci., Polym. Chem.*, 1995, **33**, 999.