View Article Online / Journal Homepage / Table of Contents for this issue

Synthesis and properties of liquid crystalline aniline monomers and semiconducting polyaniline with mesogenic side-chains

Laurence I. Gabaston,* Peter J. S. Foot and John W. Brown

School of Applied Chemistry, Kingston University, Penrhyn Road, Kingston upon Thames, Surrey, UK KT1 2EE

Novel aniline monomers substituted by mesogenic moieties with different spacer lengths are synthesised and preliminary data are reported on the conjugated polymers produced.

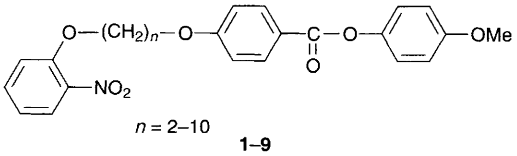
It has been shown over the last 25 years that conjugated polymers could exhibit conductivities ranging from that of undoped silicon to that of metallic copper. The most promising of these have been polyacetylene,[1] poly-*p*-phenylene,[2] polyaniline,[2] polypyrrole[2] and polythiophene.[2]

A possible way to control the conductivity of these materials may be to attach mesogenic side groups in order to confer better ordering. Some preliminary work has been reported on polythiophene,[3] polypyrrole,[4] polyacetylene[5,6] and polydiacetylene[6,7] systems. Polyaniline exhibits a much greater complexity of properties and structures[8] than most other electroactive polymers. Its electronic properties are governed by two parameters: the oxidation level and the protonation level; it possesses high conductivity in its emeraldine salt (50% oxidised and protonated) form.[9]

The first objective was to synthesise a monomer based on aniline with a side-chain mesogenic group. As aniline molecules are easily oxidised, it was decided to start by synthesising *ortho*-substituted nitrobenzenes; these were then hydrogenated to form 2-substituted anilines which were subsequently polymerised.

Firstly, a series of 4-methoxyphenyl 4-[*n*-(2-nitrophenoxy)-alkoxy]benzoates {or α-(2-nitrophenoxy)-ω-(4-methoxyphenyl-4-oxybenzoate)alkanes} (compounds **1–9**, Fig. 1) were synthesised, in order to study the influence of the number of methylene units (*n*) in the bridging group (n = 2 to 10) on the liquid crystal transition temperatures of the precursors.

These molecules were synthesised by etherification of 2-nitrophenol with an excess of the appropriate *n*-dibromoalkane (56–76% yield). The 2-(*n*-bromoalkoxy)nitrobenzenes {or α-bromo-ω-(2-nitrophenoxy)alkanes} formed were etherified with ethyl 4-hydroxybenzoate to yield ethyl 4-[*n*-(2-nitrophenoxy)alkoxy]benzoates {or α-(4-ethylbenzoate-oxy)-ω-(2-nitrophenoxy)alkanes} (60–89% yield). The esters were hydrolysed in alkaline medium to give the acids (84–94% yield), which were esterified with 4-methoxyphenol, forming the liquid crystalline molecules **1–9** (80–96% yield). Investigation of these compounds by hot-stage optical polarizing microscopy and differential scanning calorimetry revealed a strong odd–even effect of chain length on the transition temperatures.[10] The molecules with even spacer lengths were liquid crystalline above ambient temperature (Schlieren and homeotropic textures of the monotropic nematic phase), whereas the odd members were not. Hydrogenation of these molecules to form *ortho*-substituted anilines was carried out. The anilines exhibited similar liquid crystalline behaviour, but after polymerisation, no mesogenic properties were observed. The large *ortho*-substituents were simply found to lower the polymer backbone glass transition temperatures (T_g) by between 50 and 80 °C.



1–9

Fig. 1 Compounds **1–9**

Syntheses of molecules with higher liquid crystal transition temperatures and with fixed spacer groups were then devised (Fig. 2), in order to form polymers with liquid crystalline properties above their T_g.

Compound **10** was prepared by esterification of 4-[6-(2-nitrophenoxy)hexoxy]benzoic acid {or α-(4-benzoic acid-oxy)-ω-(2-nitrophenoxy)hexane} with 4-cyano-4′-hydroxybiphenyl (93% yield). Compound **11** was prepared by etherification of 2-(6-bromohexoxy)nitrobenzene {or α-bromo-ω-(2-nitrophenoxy)hexane} and 4-cyano-4′-hydroxybiphenyl (89% yield), which was then acid-hydrolysed to form the carboxylic acid **12** (88% yield); this was esterified with 4-hydroxybenzonitrile to yield compound **13** (69% yield) or 4-methoxyphenol to yield compound **14** (34% yield). All of these molecules showed liquid crystalline properties (Table 1) with high transition temperatures for molecules **10**, **12**, **13** and **14**.

After hydrogenation, polymerisation of the aniline monomers was performed by oxidative chemical polymerisation in a Brönsted acid medium.[9] Typically, this leads to a predominantly *para*-linked head-to-tail polymer which is partly proto-

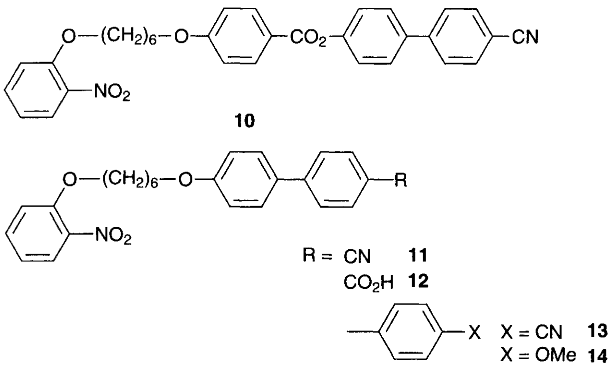


Fig. 2 Compounds **10–14**

Table 1 Transition temperature (°C) for compounds **10–14**

Compound	C-I/N† C-S‡	N-I	S_C§-N S_A¶-N	S_1-S_C§ S_1-S_A¶	N-C S_1-C*/S_2**
10	125†	199.8	—	—	66.3
11	95.3	55.3	—	—	—
12	157.3‡	227.3	214§	175.7§	146**
13	136†	190.1	—	—	65
14	134.6‡	181.4	115.2¶	72.5¶	36.8*

S_1 and S_2 phases have not been identified, but are under X-ray investigation.

Table 2 UV–VIS spectra of polymers of compounds **10**, **12** and **13** in different conditions

UV–VIS spectra	Conditions	λ_{max}/nm 2nd $\pi \rightarrow \pi^*$	λ_{onset} 1st $\pi \rightarrow \pi^*$/nm (E_g/eV)	λ_{max}/nm $\pi \rightarrow P_2$	λ_{max}/nm $P_1 \rightarrow P_2$
10	$CHCl_3$		361 (3.44)	540	—
	film $CHCl_3$	—	367 (3.38)	515	—
12	conc. H_2SO_4	247	400 (3.10)	495	682
	DMF	—	331 (3.75)	509	—
	$CHCl_3$	—	345 (3.60)	504	—
13	conc. H_2SO_4	258	396 (3.13)	483	600
	DMF	—	360 (3.45)	—	—
	$CHCl_3$	241	349 (3.56)	433	—
	film $CHCl_3$	—	382 (3.25)	—	—

nated at the nitrogen atoms. Introduction of large substituents on the aniline rendered the monomers insoluble in acidic aqueous media, so a surfactant (4-dodecylbenzenesulfonic acid) was used to disperse a chloroform solution of the monomers in aq. HCl (1 mol dm^{-3}).

Studies by cyclic voltammetry (still in progress) are consistent with the oxidation of the aniline unit to form an emeraldine-type product, with its characteristic redox system shifted to slightly higher potentials. No oxidation of the cyanobiphenyl or other mesogens appears to occur within the potential range required for polymerisation; moreover, the mesogenic groups on the nitro-intermediates show no tendency to oxidise under the conditions used. Gel permeation chromatography measurements on solutions of the products in DMF showed a wide range of molecular weights, ranging from oligomers to higher polymers (from dimers to n = 10–15). A predominantly head-to-tail coupling for the higher polymers is inferred from the IR spectra being entirely consistent with a poly(benzeneamine-quinonediimine) structure, rather than with one having significant contributions from azo-biphenyl units due to head-to-head linkages. For the lower molecular weight species, we have obtained satisfactory solution-phase NMR spectra, and have seen no sign of head-to-head products (*e.g.* benzidines) under the pH conditions used. A fuller report on the NMR and other structural characterisation of the polymers will appear elsewhere.[10]

Hot-stage polarised optical microscopy of the polymers from compounds **12** and **13** revealed Schlieren textures which flashed when subjected to mechanical stress, providing evidence of liquid crystalline behaviour. Preliminary 2-electrode measurements showed an increase in electronic conductivity for the carboxylic acid polymer with increasing temperature (at 20 °C $\sigma = 10^{-5}$ S m^{-1}, and at 220 °C $\sigma = 10^{-3}$ S m^{-1}), but the high transition temperatures of these molecules resulted in the loss of HCl protonation above 130 °C. In the case of the ester, room temperature conductivity of the protonated polymer was 10^{-3} S m^{-1}. UV–VIS spectroscopy data are shown in Table 2. The average band gap determined from thin film spectra was 3.3 eV, which is relatively high compared with that of poly(2-methoxyaniline) (3.0 eV[11]). This can be explained by the large size of the mesogenic group, the steric effect of which presumably causes twisting of the polymer backbone and results in less effective conjugation.

Studies of the effects of magnetic alignment on the polymer structure and electronic properties will be reported in due course.

Footnote

† *IR spectral data* for polymer derived from **10**: ν/cm^{-1} 3449 (2° amine NH), 3080 (arom. CH), 2925, 2854, 2228 (C≡N), 1734 (ester C=O), 1602 and 1498 (benzenoid and quinoid C=C), 1261, 1186 and 1057 (ether C–O–C), 827 (δ_{oop} CH, 1,4-disubstd. benzene) and 764 (δ_{oop} CH, 1,2,4-trisubstd. benzene), 692. For polymer derived from **12**: ν/cm^{-1} 3422, 3050, 2939, 2862, 1684 (ν C=O acid), 1603, 1498, 1249, 1188, 1167, 999, 829 and 775.

References

1 H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1977, 578.

2 *Handbook of Conducting Polymers*, ed. T. A. Skotheim, vols. 1 and 2, Marcel Dekker, New York, 1986.

3 M. R. Bryce, A. D. Chissel, J. Gopal, P. Kathirgamanathan and D. Parker, *Synth. Met.*, 1991, **39**, 397; C. Thobie-Gautier, Y. Bouligand, A. Gorgues, M. Jubault and J. Roncali, *Advan. Mater.*, 1994, **6**, 138; H. Awaji, J. Takada and M. Koshioka, Jpn. Kokai Tokkyo Koho, Jpn. Pat. 05 320 322 [93 320 322], 1993; H. Awaji, J. Takada and M. Koshioka, Jpn. Kokai Tokkyo Koho, Jpn. Pat. 05 279 457 (93 279 457), 1993; N. Koide, Jpn. Kokai Tokkyo Koho, Jpn. Pat. 06 321 935 (94 321 935) 1994.

4 P. J. Langley, F. J. Davis and G. R. Mitchell, *Mol. Cryst. Liq. Cryst.*, 1993, **236**, 225; H. Awaji, J. Takada and M.Koshioka, Jpn. Kokai Tokkyo Koho, Jpn. Pat. 05 331 266 (93 331 266) 1993; M. Mauzac, F. Vicentini, J. Barrouillet, R. Laversanne, J. P. Parneix, personal communication, 1994; P. Ibison, P. J. S. Foot and J. W. Brown, *Synth. Met.*, 1995, in the press.

5 F. Vicentini, M. Mauzac, R. Laversanne, P. Pochat and J. P. Parneix, *Liq. Cryst.*, 1994, **16**, 721.

6 J. Le Moigne, A. Soldera, D. Guillon and A. Skoulios, *Liq. Cryst.*, 1989, **6**, 627.

7 J. Tsibouklis, A. R. Werninck, A. J. Shand and G. H. W. Milburn, *Liq. Cryst.*, 1988, **3**, 1393.

8 A. P. Monkman, D. Bloor, G. C. Stevens and J. C. H. Stevens, *J. Phys. D.*, 1987, **20**, 1337; A. J. Epstein, A. G. MacDiarmid, in *Science and Applications of Conducting Polymers*, ed. W. R. Salaneck and D. T. Clark, 1990, 141; E. W. Paul, A. J. Ricco and M. S. Wrighton, *J. Phys. Chem.*, 1985, **89**, 1441.

9 E. M. Genies and M.Lapkowski, *J. Electroanal. Chem.*, 1987, **220**, 67; A. G. MacDiarmid and A. J. Epstein, *Faraday Discuss. Chem. Soc.*, 1989, **88**, 317; P. J. S. Foot and R. Simon, *J. Phys. D*, 1989, **22**, 1598.

10 L. I. Gabaston, P. J. S. Foot and J. W. Brown, submitted to *J. Mater. Chem.*

11 D. Macinnes and B. L. Funt, *Synth. Met.*, 1988, **25**, 235.

Received, 18th July 1995; Revised Manuscript Received, 17th October 1995; Com. 5/07603J