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SYNTHETIC ROUTES TO POLYPYRROLES WITH PENDANT MESOGENIC GROUPS

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Abstract A synthetic pathway is described which leads to the formation of pyrrole with a pendant aromatic groups in the β-position. Such materials are found to exhibit a monotropic liquid crystal phase. β-Substituted pyrroles of this type may be polymerised chemically to form poly(β-substituted pyrroles).

INTRODUCTION

Conductivity in conjugated polymers is a well known and much studied phenomenon. A wide range of conducting polymers have been synthesized including, polyacetylene[1] Poly(*p*-phenylene)[2] polythiophene[3] and polypyrrole[3]. Such materials are of particular interest, both in terms of basic science, and for potential applications extending from lightweight components in fuel cells, to materials for non-linear optics. Recently considerable attention has been devoted to the production of materials which combine the inherent advantages of a conjugated backbone with processibility.[4,5] The most common and most successful approach to this objective is to attach pendant side groups to the aromatic system. Thus, for example polymers based on acetyl benzene[4] and β-decylpyrrole[5] have been prepared and shown, in their undoped states at least, to be soluble. One extension to this idea, which offers intriguing potential for the production of materials with improved properties is to incorporate side groups which, in addition to improving the processibility of conducting polymer systems, offer the potential for mesophase formation. One such system, based on poly(thiophene) has been reported[6] and found to exhibit a liquid crystal phase, in combination with conductivities of 1.5×10^{-2} Scm^{-1}. In this contribution we describe a synthetic pathway to pyrrole based systems which contain aromatic side groups of the type expected to give rise to mesophase formation. It was intended that the presence of a mesophase could be utilized to improve the properties of pyrrole based polymers, by for example increasing the level of order, which is known to improve conductivity.[7]

SYNTHESIS DESIGN

Scheme 1 shows the synthetic pathway towards a liquid crystalline pyrrole. The ultimate aim of these investigations was the synthesis of a substituted pyrrole which could be converted into a conducting polymer.

Clearly to allow the formation of polypyrrole the substituent must be in the β(3)-position, as the α(2)-sites must be left free for the polymerisation process. Unfortunately the natural site for electrophilic attack in pyrrole is at the α-position; however this problem can be circumvented by initial conversion to the N-tosyl pyrrole (readily achieved by the reaction of potassium pyrrole with tosyl chloride).[6] Friedel-Crafts acylation then occurs regiospecifically in the β-position. In the route described here it was found that the tosylate group was best removed at this stage to avoid complications in the next step. The mesogenic unit, in this case cyanobiphenol (although other phenolic mesogens would also be suitable, provided they were stable in weak base), is readily attached to the pendent alkyl chain *via* a Williamson synthesis using potassium carbonate in dimethylformamide. The resultant acyl pyrrole, was reduced to the alkyl pyrrole using sodium borohydride in hot propan-2-ol.[8]

EXPERIMENTAL

N-tosyl pyrrole was prepared from the reaction of potassium pyrrole with tosyl chloride using an established procedure.[9] The low molecular weight liquid crystal 4-cyano-4'-*n*-hexyloxybiphenyl (M18) was obtained from BDH Ltd. All materials were characterised by infra-red, mass spectroscopy and ^{1}H nmr. The reactions described in Scheme 1 were as performed as follows:

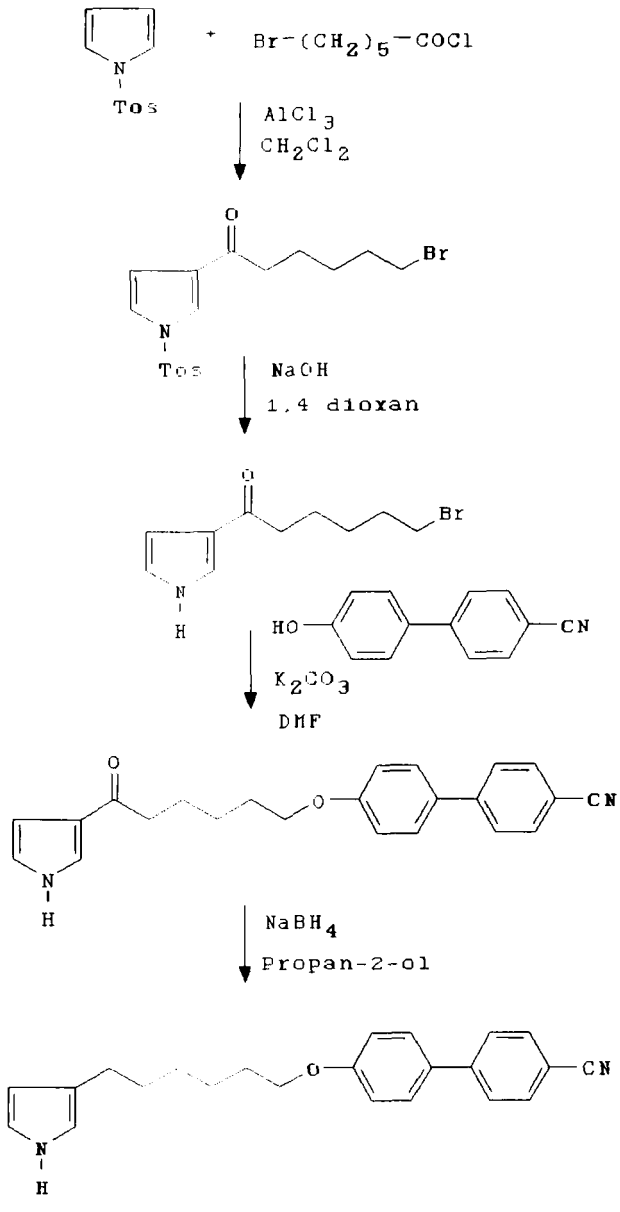
Preparation of N-tosyl-3-(6-bromohexanoyl)pyrrole

Anhydrous aluminium chloride (21.7 g, 162 mmol) was added to dry CH_2Cl_2 (400 ml) and stirred under a nitrogen atmosphere. 6-Bromohexanoyl chloride (30.0 g, 140 mmol) in CH_2Cl_2 (300 ml) was added dropwise at 20°C and the solution allowed to stir for 30 min. N-tosyl-pyrrole (24.1 g, 109 mmol) in CH_2Cl_2 (300 ml) was slowly added dropwise, keeping the temperature below 5°C. The reaction was left to stir under a nitrogen atmosphere for *ca.* 20 hours, after which it was carefully hydrolysed with ice-water, and the aqueous layer extracted with dichloromethane. This solution was washed with brine and dried over magnesium sulphate. Filtration followed by evaporation of the solvent yielded a dark brown oil which crystallised upon standing. The product was used without further purification.

3-(6-bromohexanoyl)pyrrole.

The crude product, N-tosyl-3-(6-bromohexanoyl)pyrrole , was dissolved in a mixture of 1,4-dioxane (500 ml) and aqueous NaOH (5M, 500 ml) and

stirred at room temperature for 2 days. The dioxane was removed and the pale yellow solid dissolved in dichloromethane. After washing with brine, drying and filtering, the solvent was removed to yield a pale yellow oil which crystallised on cooling. The yield of crude product was 19.7 g (74.1 %, based on N-tosylpyrrole). The product was recrystallized from diethyl ether/petroleum ether to give white crystals mpt. 73.5-76°C.



Scheme 1

3-[6-(4'cyanobiphenyl-4-oxy)hexanoyl] pyrrole

3-(6-bromohexanoyl) pyrrole (8.00 g, 32.8 mmol), 4-cyano-4'-hydroxy biphenyl (6.39 g, 32.7 mmol), anhydrous potassium carbonate (13.83 g, 100.0 mmol) and potassium iodide (trace) were added to DMF (165 ml) and warmed to 90-100°C for one hour. The product was precipitated from solution by the addition of a large excess of water and filtered at the pump. The cream solid was dried at the pump and then in vacuo over P_2O_5 at 65°C overnight. The crude product (10.1 g, 86.0 %) was recrystallised from aqueous isopropanol (mpt. 131.0°C).

3-[6-(4'-cyanobiphenyl-4-oxy)hexyl] pyrrole

3-[6-(4'-cyanobiphenyl-4-oxy)hexanoyl] pyrrole (4.64g, 13 mmol) and sodium borohydride (5.29g, 0.1398 mmol) were added to propan-2-ol (150ml) and the solution refluxed for 48 hours. The reaction was hydrolysed with brine and the organics extracted with ethyl acetate (5 portions). The combined organics were washed once with fresh water, dried over magnesium sulphate, filtered and the solvent removed to yield the crude product (yield 2.92 g, 65.5 %). The product was purified by recrystallisation from ethyl acetate /petroleum ether. The phase behaviour of this material is reported below.

Chemical polymerisation was performed using the method of Kaneko *et al*[10]. Stable solutions of the 3-substituted monomers and ferric chloride in dichloroethane/methanol were cast onto glass slides, whereupon evaporation of the solvents gave thin and brittle self-supporting films. The films were reduced by stirring in aqueous 2% hydrazine solution.

RESULTS AND DISCUSSION

Phase behaviour

The phase behaviour of 3-[6-(4'-cyanobiphenyl-4-oxy)hexyl] pyrrole was monitored using optical microscopy between crossed polars. Although no liquid crystal phase could be detected on heating, on cooling the sample from the isotropic melt, a monotropic nematic phase was observed. Thus on heating the isotropic phase was attained at 96.6°C; on cooling a nematic phase could observed (with the appropriate cooling conditions) when the temperature came down to 72.6°C. Crystallisation was observed when the temperature fell below 60.1°C. In contrast the unreduced form, 3-[6-(4'-cyanobiphenyl-4-oxy)hexanoyl] pyrrole, showed no evidence of any mesophase, and melted at 132.0°C.

The formation of monotropic liquid crystal phases clearly presents difficulties in the utilization of the mesophase for forming conducting polymers. In this sense the monomer described here is inferior to analogous thiophene derivatives. The low stability of the phase in the pyrrole case is presumably due to the availability of the N-H unit for intermolecular hydrogen bonding;[11,12] in the case of thiophene derivatives such interactions are not possible. It was found however, that the stability of the mesophase could be considerably enhanced by the addition

of a proportion of a commercially obtained liquid crystalline material M18. This is illustrated by the DSC traces shown in Figure 1; for a sample where 10% of the low molecular weight liquid crystal M18, the mesophase is monotropic and exist over only some 10°C; for the mixture containing 25% of M18, in contrast, the liquid crystal phase was found to be stable over the whole temperature range studied.

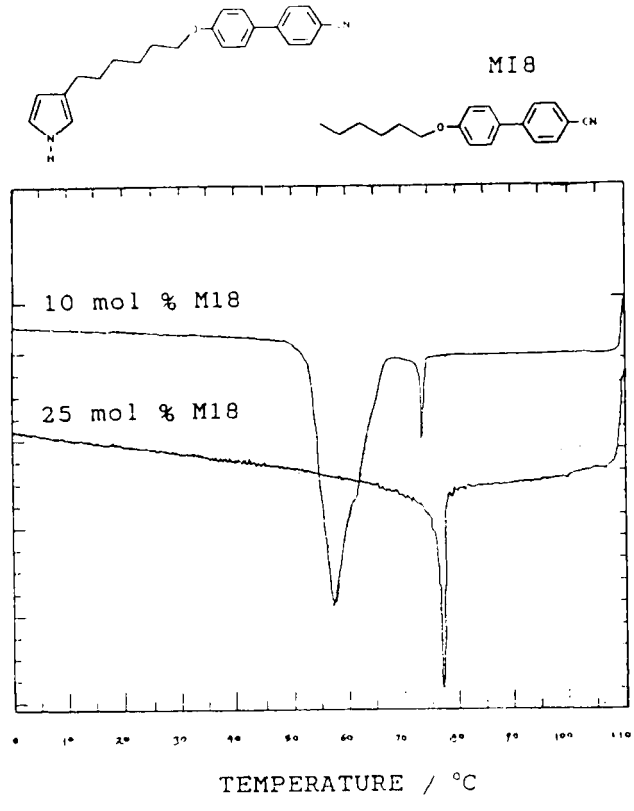


Figure 1

Polymerisation

3-[6-(4'-cyanobiphenyl-4-oxy)hexyl] pyrrole was found to be readily polymerised chemically, using the method outlined above.[10] The films obtained were black and exhibited no phase behaviour, up to 400°C, either in the reduced or in the oxidized form. However, some limited solubility was apparent for the undoped poly(pyrrole) system in dimethyl formamide.

CONCLUSION

β-Substituted pyrroles with pendant mesogenic units may be synthesized, however, the stability of the mesophase is apparently reduced by the presence of hydrogen bonding.[11,12] This makes the use of a liquid crystalline phase to organize pyrrole systems rather more difficult than with polythiophenes.[6] However, relatively stable liquid crystal phases may be achieved *via* mixing with small quantities of a material with a stable liquid crystal phase. The polymers obtained from the monomer discussed here exhibited no mesophase, but limited

solubility. The use of the liquid crystal phase to form ordered polymers *via* aligned monomers is the subject of current studies.

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