

Formation of polypyrrole from 2,5-bis(2-pyrrolyl)pyrrolidine†

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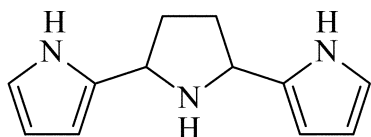
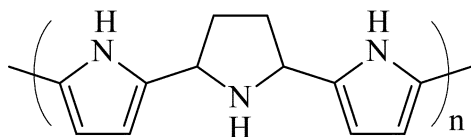
Received (in Cambridge, UK) 9th October 2003, Accepted 8th December 2003

First published as an Advance Article on the web 13th January 2004

2,5-Bis(2-pyrrolyl)pyrrolidine has been found to spontaneously polymerize under acidic conditions in the presence of air to produce fully aromatic polypyrrole.

Polypyrrole has attracted widespread scientific interest for more than 30 years.¹ It is usually prepared from pyrrole by chemical or electrochemical oxidation.^{1,2} However, these processes produce poorly defined materials with a variety of different linkages and oxygenated defects (ketones, alcohols, *etc.*).²⁻⁴ There has therefore been interest in the use of more controlled coupling processes, such as Stille and Ullmann coupling,^{2,5,6} although the synthetic challenges of such processes have severely restricted work in this area. There is still a need for a convenient route to well defined polypyrrole.

2,5-Bis(2-pyrrolyl)pyrrolidine (**1**)⁷ is an attractive precursor for polypyrrole for a number of reasons. Firstly, it already contains the α - α linkages required in properly conjugated polypyrrole. Secondly, the electronically isolated terminal pyrrole rings will be most reactive during polymerization at the desired α -positions with little reactivity at the β -positions. In contrast, the reactivity at the β -positions of the fully conjugated trimer, 2,2': 5',2''-terpyrrole, is only slightly less than at the α -positions.^{8,9} Thirdly, the polymerization of **1** offers the possibility of producing a processable non-conjugated precursor polymer, **2**, which can be subsequently converted to fully conjugated polypyrrole.

**1****2**

When dissolved in aqueous acid, **1** polymerizes spontaneously to produce highly conjugated polypyrrole, as shown by the electronic absorption spectra in Fig. 1. The absorbance at 217 nm due to **1** decreased with time, and was replaced by a new major peak due to polypyrrole¹⁰ at 438–441 nm. The low energy of the polypyrrole band indicates that a highly conjugated polymer is formed. The absorbance maximum is lower in energy than the absorbance of the “virtually defect-free” polypyrrole reported by Zotti *et al.*¹⁰

† Electronic supplementary information (ESI) available: details of the synthesis of 2,5-bis(2-pyrrolyl)pyrrolidine and polypyrrole. See <http://www.rsc.org/suppdata/cc/b3/b312660a/>

Other features of the spectra in Fig. 1 provide insight into the mechanism of the formation of polypyrrole from **1**. The reaction must involve two main steps: polymerization and dehydrogenation of the central ring. If polymerization occurs first, then an intermediate containing bipyrrrole linkages will be formed. This would exhibit a λ_{max} close to 276 nm.¹⁰ On the other hand, dehydrogenation prior to polymerization would produce 2,2': 5',2''-terpyrrole ($\lambda_{\text{max}}^{10} \sim 317$ nm) as an intermediate.

The spectrum obtained at *ca.* 5 min shows a peak at 317 nm that can unambiguously be attributed to terpyrrole, but there is no evidence of a bipyrrrole intermediate. Clearly dehydrogenation of **1** is faster than its polymerization under the conditions of this experiment (very low concentration; 20% HCl). As the polypyrrole peak grows, the terpyrrole concentration remains low and steady, indicating that its polymerization is relatively fast. With time, a peak at *ca.* 280–290 nm does develop, indicating that there is some polymerization or oligomerization of **1** in parallel with its dehydrogenation. This peak is much more pronounced when the reaction is conducted with higher concentrations of **1**, under less acidic conditions, or by using Fe³⁺ as the oxidizing agent. Thus, with appropriate selection of conditions it should be possible to isolate the non-conjugated precursor polymer, **2**.

The formation of polypyrrole from terpyrrole should involve intermediates containing 6, 9, 12, *etc.* conjugated pyrrole rings. Based on the inverse relationship between λ_{max} and the number of rings, established by Zotti *et al.*,¹⁰ the first three of these compounds would exhibit λ_{max} values of *ca.* 375, 390, and 400 nm, respectively. The absence of peaks at these wavelengths in the spectra in Fig. 1 show that these intermediates react rapidly to produce polypyrrole. It also reaffirms the high degree of polymerization indicated by the position of the polypyrrole absorption.

The polymeric material formed initially from **1** is soluble, indicating that it either has a relatively low molar mass and/or that it is protonated at non-aromatic defects. With time, the polymer begins to precipitate as a black solid. An infrared spectrum of the solid product collected from an experiment in which Fe(III) was added as an oxidant is shown in Fig. 2. The bands at 1620 and 1576 cm⁻¹ can be attributed to the stretching of conjugated C=C bonds in the polypyrrole structure.^{11,12} The higher frequency band indicates the presence of chain segments with a low degree of

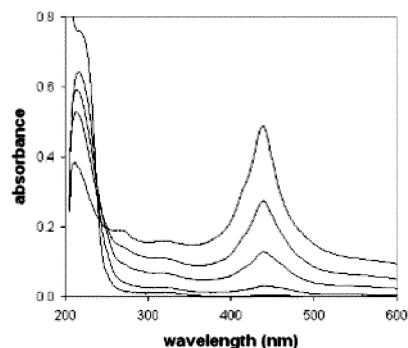


Fig. 1 Electronic absorption spectra of **1** (30 μM) in 20% HCl(aq) recorded over a period of 30 h (at *ca.* 0.1, 2, 6, 11 and 30 h). The absorbance at *ca.* 210 nm decreased with time, while all absorbances at longer wavelengths increased. Air was not excluded from the reaction mixture.

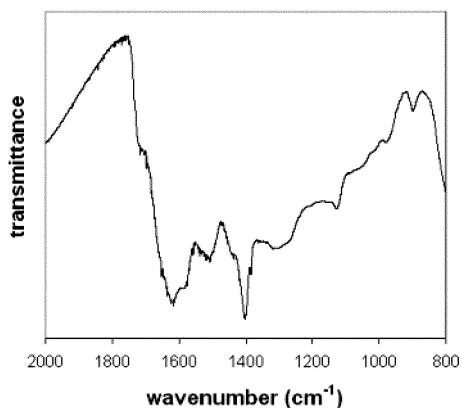


Fig. 2 IR spectrum (KBr disc) of a sample of polypyrrole prepared by treating **1** (20 mM) with FeCl_3 (0.6 mM) in 40 ml 20% HCl for 1 day.

conjugation.¹² These are presumably associated with the carbonyl defects that give rise to the 1702 cm^{-1} band,³ and/or breaks in conjugation due to pyrrolidine rings. The bands at 1438 (C-N str.) , $1307\text{ (C-H and N-H def.)}$, $1266\text{ (C-N str. and C-H def.)}$, and *ca.* $1050\text{ (C-H def.) cm}^{-1}$ are close to the characteristic values reported for polypyrrole.^{11,12} The strong additional band at 1402 cm^{-1} may be due to pyrrolidine defects.

Although further work is needed to optimize the synthesis of polypyrrole from **1** and to isolate and characterize the non-conjugated intermediate, **2**, the results presented here indicate that there is potential for producing well defined polypyrrole from **1**. The solubility of the initially formed polymers or oligomers is

particularly important, since it will allow their proper characterization. Lack of solubility has been a serious obstacle in polypyrrole research since its inception, and has resulted in the almost ubiquitous use of poorly characterized materials. New, soluble and well characterized materials could be used directly in applications, or subsequently be converted to insoluble materials.

This work was supported by the Natural Sciences and Engineering Research Council of Canada and Memorial University. AG thanks Deutscher Akademischer Austausch Dienst e.V. for financial support.

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