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Synthesis and properties of polypyrrole annelated with bicyclo[2.2.2]octene units

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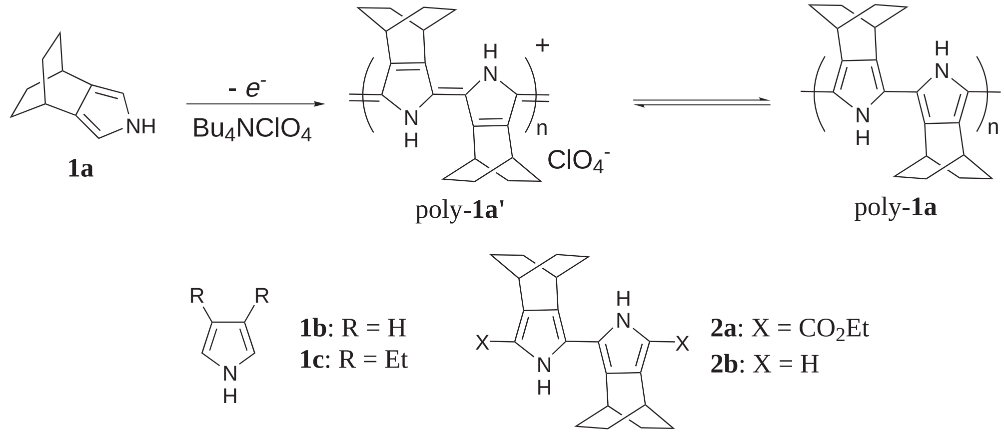
Abstract—Polypyrrole annelated with bicyclo[2.2.2]octene provides a new material that possesses a raised HOMO band, extended conjugation and a rigid porous structure. © 2001 Elsevier Science Ltd. All rights reserved.

In order to develop new functions or properties of polypyrroles, pyrroles with various substituents at the β- or *N*-position have been used so far.[1] However, the introduction of such substituents into the pyrrole rings affects the morphology and conformation of polypyrroles. It is generally appreciated that the morphology of conductive polymers plays a fundamental role in defining the characteristics of the material. The morphology of polypyrrole films depends on various factors such as dopant anions, film thickness and substituents of pyrroles.[2] The morphology and conformation of polypyrrole film derived from unsubstituted pyrrole are intractable because the film contains many structural defects derived from the α,α- and α,β-coupling. In general, doped states of polypyrroles contain π- or σ-dimers,[3] which make the morphology very complicated. It is essential to minimize such ambiguities of polypyrroles to allow fine tuning of their properties. In this paper we propose a new strategy to control the properties of polypyrroles, which is based on bicycloannelation of polypyrroles such as **2** depicted in Scheme 1. The rigid bicyclic ring may prevent π- or σ-dimerization of polypyrroles and also α,β-coupling of pyrroles. Furthermore, bicyclo[2.2.2]octene ring systems may be less sterically demanding than other alkyl groups.[4] Komatsu and co-workers have demonstrated that con-



Scheme 1.

Keywords: polypyrrole; bicyclo[2.2.2]octene unit; morphology of polypyrrole.

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jugated systems fused with bicyclo[2.2.2]octene units are stabilized in their cations or radical cations by σ–π conjugation.[5] Therefore, the doped states of polypyrroles should be stabilized by annelation with the bicyclo[2.2.2]octene units, and such polypyrroles may provide a new material with good conductivity and stability.

The electrochemical properties of **1a**[6] were studied by cyclic voltammetry (CV). Fig. 1 shows the cyclic voltammograms corresponding to the electropolymerization of **1a**, pyrrole (**1b**) and 3,4-diethyl pyrrole (**1c**). The CV was carried out on a Pt disk electrode for CV with 3×10^{-3} mol dm^{-3} of monomer and 0.1 mol dm^{-3} of tetrabutylammonium perchlorate at a scan rate of 200 mV s^{-1} in MeCN. Repetitive cycling leads to the emergence of reversible peaks at $E_{pa}=-0.36$ V and $E_{pc}=-0.49$ V (versus Ag/AgNO$_3$) for **1a**, where peak separation DE$=E_{pa}-E_{pc}$ is 0.13 V. In the case of polymerization of **1b**, irreversible peaks at $E_{pa}=-0.07$ V and $E_{pc}=-0.29$ (DE$=0.22$ V) were obtained. Repetitive cycling of **1c** leads also to reversible peaks at $E_{pa}=-0.22$ V and $E_{pc}=-0.30$ V (DE$=0.08$ V). The apparent electrochemical reversibility was seen to be higher for poly-**1a** and poly-**1c** than for poly-**1b** from CV, indicating that the counter ion ClO_4^- moves more easily in poly-**1a** and poly-**1c** than in poly-**1b**. It is worth noting that the oxidation potential of poly-**1a** is much lower than that of any other polypyrrole. For example, the oxidation potential of poly-**1a** is more negative than that of a polymer of 3,4-dimethoxypyrrole ($E_{pa}=-50$ mV versus Ag/AgCl, which corresponds to $E_{pa}=-0.29$ V versus Ag/AgNO$_3$).[7] This result is in good agreement with the results of other π-conjugated systems fused with bicyclo[2.2.2]octene units reported by Komatsu, where the bicyclo units are demonstrated to be more effective than alkoxy groups for raising the HOMO energy levels of polypyrrole.[5] The HOMO level of monomer **1a** (E_{pa} of **1a**$=0.74$ V) is lower than that of **1c** (E_{pa} of **1c**$=0.67$ V). Thus, the bicyclo[2.2.2]octene unit at the 3 and 4 positions does not raise the HOMO energy of the corresponding pyrroles or thiophenes. However, this group is very effective for raising the HOMO energy levels of the corresponding polymer. This result suggests the bicyclo[2.2.2]octene units stabilize the quinoid forms in doped polypyrroles.

The rigid framework of bicyclic units may help to fix the *anti*-periplanar conformation of the polypyrroles to extend the effective conjugation. It is well known that the conformation of poly- or oligopyrroles depends on the substituents of the pyrrole rings.[8] There is a good correlation between the absorption wavelengths in the absorption spectra of 2,2′-bipyrroles and the twist at the 2,2′-bond of bipyrroles. The UV–vis data of monopyrroles, dipyrroles and polypyrroles are summarized in Table 1. Evidently, the magnitude of red-shift and absorption strength (ε) associated with the dimerization of pyrrole **1a** is larger than that in the case of 3,4-diethylpyrrole. Thus, the bicyclo[2.2.2]octene framework is very effective in fixing the conformation of dipyrroles or polypyrroles to maximize the π-conjugation. This is due to the rigidification of the conformation of polypyrroles by annelation with bicyclo[2.2.2]octene units. Rigidification of the π-conjugated system by covalent bridging is one reliable method for reducing the band gap (E_g).[9] Annelation of pyrroles with the bicyclo[2.2.2]octene framework provides an alternative method for rigidifying the π-conjugated system. A single crystal X-ray diffraction analysis of β-substituted terpyrroles shows the twisted helical structure in the solid state.[10] A polymer of 3,4-diethylpyrrole also forms a twisted helical conformation to reduce the effective conjugation between the adjacent pyrrole units. On the other hand, the π-conjugation of poly-**1a** can be extended due to the co-planar conformation between the repeated units of conjugated polymers. The conductivity of doped polypyrroles was as follows: poly-**1b** (1.0–500 S cm^{-1}), poly-**1a** (0.1 S cm^{-1}) and poly-**1c** (0.001 S cm^{-1}), respectively. Thus, the present results show clearly that the conductivity of polypyrroles involves transport of the charge carriers both along the polymer backbone for poly-**1a** and across neighboring chains for poly-**1b**. Neither path allowed poly-**1c** to

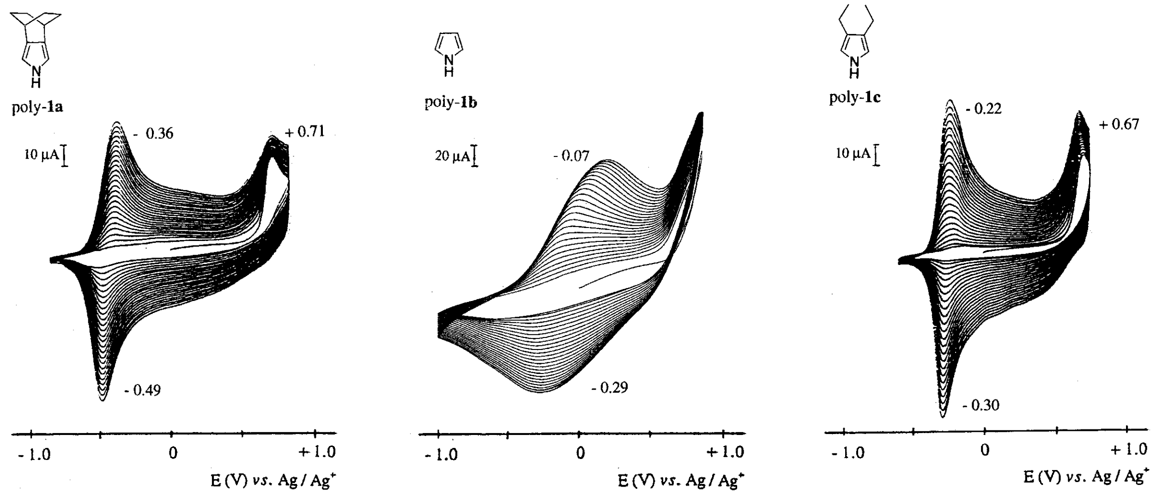
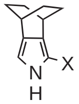
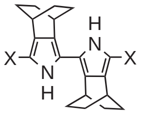
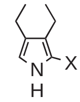
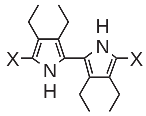
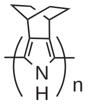


Figure 1. Cyclic voltammograms of **1a**–**c** (2–3 mM) in presence of *n*-Bu$_4$NClO$_4$ (0.1 M) in MeCN; scan rate: 200 mV s^{-1}.

Table 1. UV–vis data of pyrroles, dipyrroles and polypyrroles

Compound		λmax (ε)/nm
	X = CO_2Et	270 (9,700)[a]
	X= H	217[b]
	X = CO_2Et	337 (21,400)[a]
	X= H	275[b]
	X = CO_2Et	272 (9,100)[a]
	X = H	223[b]
	X = CO_2Et	314 (17,200)[a]
	X = H	252[b]
	poly-**1a** (in $CHCl_3$)	340 (E_g = 2.4 eV)[c]

[a] In chloroform. [b] In hexane. [c] Band gap (E_g) was determined by absorption edge (520 nm).

exhibit low conductivity of doped poly-**1c**. Although more studies are necessary, the present study and other information in the literature suggest that interchain hopping may be the most important factor for transport of the charge in polypyrroles or other conductive polymers.[1]

The in situ atomic force microscopy (AFM) images of polymer film derived from **1a** and **1b** are shown in Fig. 2. Poly-**1b** has a more globular surface than poly-**1a**, and the surface roughness is larger for poly-**1b** than for poly-**1a**. Thus, the morphology of poly-**1a** is very different from that of poly-**1b** in which many structural defects are involved.[11]

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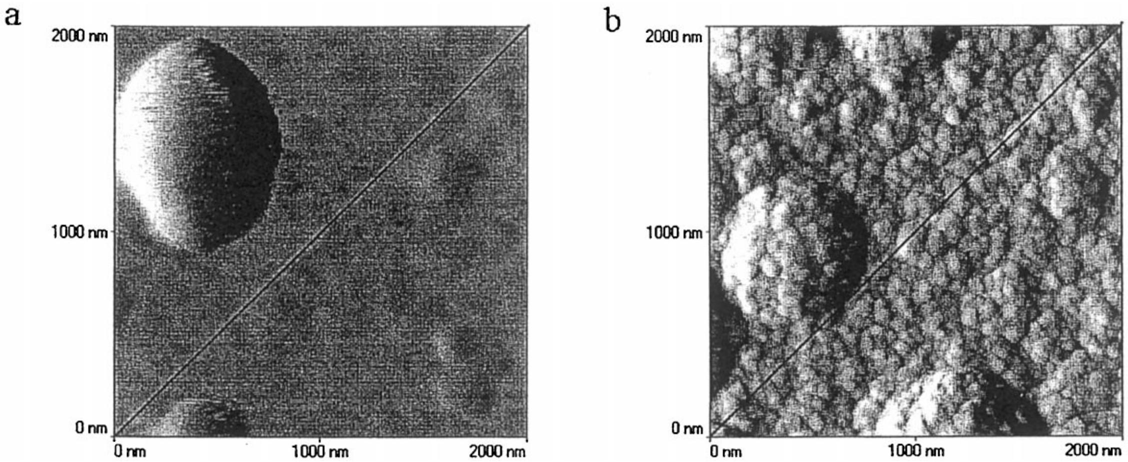

Figure 2. AFM images in air of (a) poly-**1a** and (b) poly-**1b** on glassy carbon electrode. The films were prepared by applying 1 V versus SCE in an MeCN solution containing 2.0 mM monomer and 0.1 M TBAP; total charge was 133 mC cm^{-2} (film thickness was estimated at 330 nm).

11. Electrochemical investigation and morphology of polypyrrole film, see: Tsai, Y. C.; Suarez, M. F.; Compton, R. G., S. Ito and N. Ono, *J. Electroanal. Chem.* **1999**, *477/1*, 25: AFM experiments were performed using a Topometrix model TMX 2010 atomic force microscope in contact model with pyramidal silicon tips (Topometrix AFM probes 1520). These images were obtained at scanning areas 2×2 μm. The used scan rate was 20 μm s^{-1}.