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Raman Characterization of Oligoaniline Self-Assembled Microspheres

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In 2006 Venâncio *et al.* [1] showed that the aqueous oxidative polymerization of aniline in mild acidic conditions leads to the formation of hollow microspheres (diameter, 1,5 - 6 μm). By elemental analysis, UV-VIS, FTIR and ^1H -NMR spectra the authors suggested a new structure with linear -N-N- linkages called polyazanes. However, according to Sapurina *et al.*, the products of aniline oxidation in the interval pH 2,5 – 4 are oligomers with phenazine cycles [2]. Surwade *et al.* believe that these products are mixtures of Michael-type adducts of benzoquinone monoimine and aniline at various stages of hydrolyses [3]. In order to investigate these apparent contradictions we performed a more detailed investigation using, in addition to the abovementioned techniques, resonance Raman, HPLC-MS, ^{13}C -NMR and Raman microscopy, comprising products obtained at five different reaction times (5.5, 22, 49, 102 and 171 hs). In Figure 1 are displayed the SEM images of 5.5 and 171 hs reaction time products showing the evolution of oligoanilines organization.

Figure 1A and 1B shows the UV-VIS and the pre-resonance Raman spectra of oligoaniline obtained after 171 hs of reaction, respectively. It is worth mentioning that the oligoanilines obtained at other reaction times showed the same spectral patterns. Following the Surwade *et al.* paper, we synthesized the model compound (AnBzq) obtained by aniline polymerization using *p*-benzoquinone as an oxidant agent. The UV-VIS and the pre-resonance Raman spectra of AnBzq are presented in Figure 1C and 1D. The comparison of both absorption and Raman spectra shows that in fact, the same chromophore is present in both compounds. This result is supported by ^1H - and ^{13}C -NMR data.

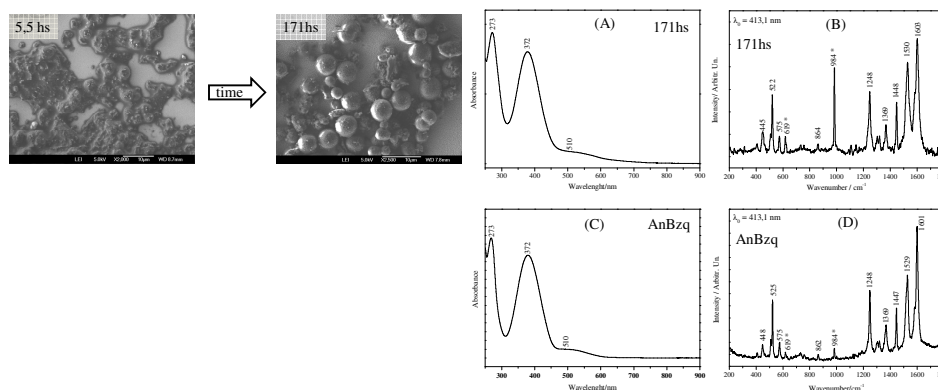


FIGURE 1. SEM images of 5.5 and 171 hs reaction time oligoanilines. (A) UV-VIS and (B) Raman spectra ($\lambda_0=413, 1 \text{ nm}$) of 171 hs reaction time oligoaniline. (C) UV-VIS and (D) Raman spectra ($\lambda_0=413, 1 \text{ nm}$) of AnBzq. The bands identified by * refer to potassium sulfate.

In order to understand the first steps of the oligoanilines formation we investigated the 5.5 hs time reaction product. The SEM and optical images (Fig. 2 A and B) shows that even in this short time reaction, it is possible to note the presence of organized microspheres (dark brown region in Fig. 2 B), although an amorphous phase (light brown region in Fig 2B) predominates. The Raman microscopy study of oligoaniline (5.5 hs) using exciting radiation at 632,8 nm shows two different spectral patterns (Figure 2D). It allowed correlating the bands 609 and 1372 cm^{-1} to the microspheres, while the bands 446 and 1680 cm^{-1} to the amorphous phase. The Raman mapping considering these bands is showed in Figure 2C.

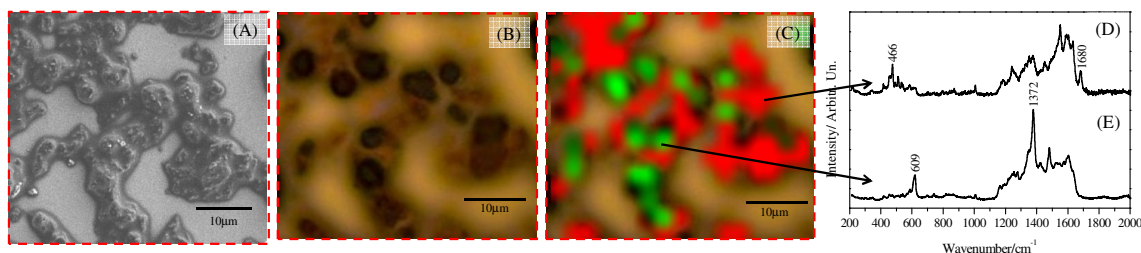


FIGURE 2. (A) SEM image, (B) Optical image, (C) Raman microscopy ($\lambda_0=632,8$ nm), the red region refers to peak intensity at 1680 cm^{-1} and the green region refers to peak intensity at 1370 cm^{-1} , (D) Raman spectra of amorphous phase and (E) Raman spectra of microspheres phase present in oligoaniline isolated at 5.5 hs of reaction.

It is interesting to note that the microspheres Raman spectral pattern is similar to the Raman spectra of phenazine-like structures (bands at 609 and 1370 cm^{-1}), [4] while the amorphous Raman spectrum is similar to AnBzq Raman spectrum (bands at 446 and 1680 cm^{-1}) as showed in Figure 1D.

The Raman microscopy study showed, at first stages of the oligoaniline reaction, the presence of two distinct compounds, where the microspheres phase was attributed to phenazine-like structures and the amorphous phase to aniline-benzoquinone adducts. Summing up, it seems that the structures proposal by Sapurina *et al.* and Surwade *et al.* are both correct.

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