Le Bail Method Used to Study Chemically Synthesized Polyanilines

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Le Bail Method or *Profile Matching* [1] inbuilt in *Fullprof* program [2] was successfully used to extract average microstructural information from polyanilines [3]. In this method the overall diffraction profile is calculated as the sum of overlapping peaks whose positions, shape functions, and intensity are defined by the unit cell parameters and half-width parameters. We report here an observation of crystalline phases in the doped and undoped polyaniline powder. ES-PANI powder exhibits broad peaks at 2θ angles around 6, 9, 11, 15, 21, 25, 27, 29, 33, 36 and 52°, which indicates some degree of crystallinity. When the ES-PANI is neutralized with NH_4OH, the diffraction peaks become progressively broader and some peaks gradually disappear, showing a decrease in the degree of crystallinity of EB-PANI. The degree of crystallinity was determined from XRD patterns using the Peak Fitting Module (PMF) program [4]. It was determined that the ES-PANI has 49% of crystallinity, while EB-PANI is less crystalline, with 32% of crystallinity. Refining using the cell parameters reported by Evain *et al*, 2002 [5], the calculated and observed diffractograms were not overlapping in the region between 5 and 14º 2θ mainly due to the presence of a small peak located at 6° 2θ. To solve this bad fitting, some changes in the cell parameters had to be done in the refinement in the following order: doubling of the b cell parameter to account for the low angle reflection; refinement of the spherical harmonics parameters, to account for anisotropic size broadening, and refinement of cell parameters. After these steps, the refinement was concentrated in the cell parameters and in the size parameters, being refined either simultaneously or separately.

Final refined cell parameters for ES-PANI are a=5.5829(5) Å; b=17.52(1) Å; c=22.852 (2) Å and Cell volume V=2209.4 (4) $Å^3$. For EB-PANI, the refined cell parameters are a=5.734 (8) Å; b=17.785 (3) Å; c=23.309 (3) Å and Cell volume V=2355.7(6) $Å^3$. The cell angles were fixed as 90°.

The average crystallite size obtained from the refinement for ES-PANI is 34(8) Å. There is a smaller apparent size of 24.02 Å in the [001] direction and almost equivalent along [010] and [100], respectively 41.91 and 38.07 Å. For EB-PANI, the average crystallite size is 27(3)Å and there is also a smaller apparent size of 22.73 Å in the [001] direction and almost identical along [010] and [100], respectively 27.85 and 28.60 Å.

[1] Le Bail, A. ; Duroy, H. ; Fourquet, J.L. Mat Res Bull, 23, 447 (1988).

[2] Rodríguez-Carvajal, *J. FullProf Program. Laboratoire Leon Brillouin (CEA-CNRS)*, version September **2007**.

[3] Bhadra,S.; Singha,N.K.; Khastgir, D. *J Appl Polym Sci*, 104, 1900 (**2007**).

[4] Microcal Origin software (version 7.5), *OriginLab Corporation,* One Roundhouse Plaza, Suite 303, Northampton, MA 01060, USA

[5] Evain, M; Quillard, S.; Corraze, B; Wang, W; MacDiarmid, A. *Acta Crystallogr E* **2002**, 58, o343.