Supporting Information to:

The Deep Impact of the Template on Molecular Weight, Structure and Oxidation State of the Formed Polyaniline

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1. The Method of Determining the Polyaniline Content in the PANI/PC Composite

The exact percentage of polyaniline (PANI) in the polycarbonate/polyaniline (PC/PANI) composites was found from the analysis of their solutions in N-methyl-2-pyrrolidone (NMP) by the UV-Vis spectroscopy method.[1] This method is based on the fact that UV-Vis spectra of PANI both in emeraldine base (EB) and leucoemeraldine base (LEB) states are completely different from UV-Vis spectrum of another component (PC) of the composite. We have chosen LEB state of PANI for the analysis by two reasons. The first one is the fact that LEB has reproducible UV-Vis spectrum due to the same units unlike PANI in EB state with frequently differing ratio of quinoid (Q) and benzenoid (B) units (Q/B). This means that a height of the LEB absorption band in its UV-Vis spectrum quantitatively displays LEB and therefore PANI concentration in the solution. The second reason is the fact that LEB better dissolves in NMP than EB by our experience. This LEB ability not only facilitates its complete dissolution from the composite even in the case of insoluble template particles, but probably minimizes in the NMP solution association of LEB macromolecules comparatively with EB macromolecules.

To prepare the PC/LEB solution we dissolve in NMP a portion of PC/PANI composite containing dedoped PANI in EB state and reduce it by adding a surplus of ascorbic acid. This reductant was successfully used earlier to reduce PANI and to estimate its oxidation state by UV-Vis spectroscopy method.[2] Applicability of our approach is well illustrated by UV-Vis spectra (Fig. S1) of the PC/PANI composite with PANI reduced to LEB by ascorbic acid (1) , ascorbic acid (2), PC (3) and NMP (4). One can see that LEB spectrum (1, peaked at 343 nm) in the composite solution practically does not overlap with spectra of other components

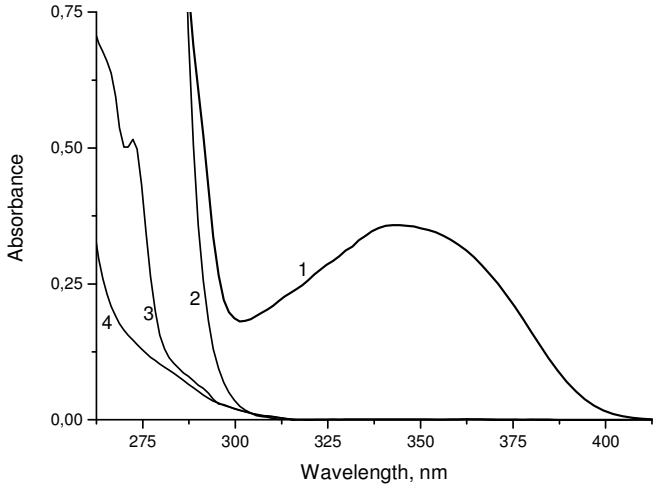

Fig. S1. UV-Vis spectra of solutions in NMP of the PC/PANI composite mixed with ascorbic acid (1), ascorbic acid (2), PC (3) and of pure NMP (4). Thickness of the quartz cuvette is 1 mm.

Typically the PC/PANI composite reduced to LEB state can be prepared as follows. The synthesized PC/PANI composite is dedoped in surplus of 0.3 wt% ammonia aqueous solution for 24 h then it filtered, washed with distilled water and finally dried in dynamic vacuum to a constant weight. 35 mg of the dry dedoped powder composite is dissolved in 15 ml of NMP and mixed with the solution of 1.5 g ascorbic acid in 5 ml in NMP. The blue solution of the PC/PANI composite with PANI in EB state becomes practically immediately almost colorless due to EB reduction to LEB state. This solution is kept for about 2 h; then it is placed in 1 mm quartz cuvette to register its UV-Vis spectrum (Fig. S1, curve 1).The spectrum contains the typical LEB absorption band. We use a height of this absorption band at 343 nm to determine concentration

of LEB (C_s) in the obtained solution with a help of the calibration curve built as a concentration dependence of the absorbance of LEB (reduced PANI) (Fig. S2).

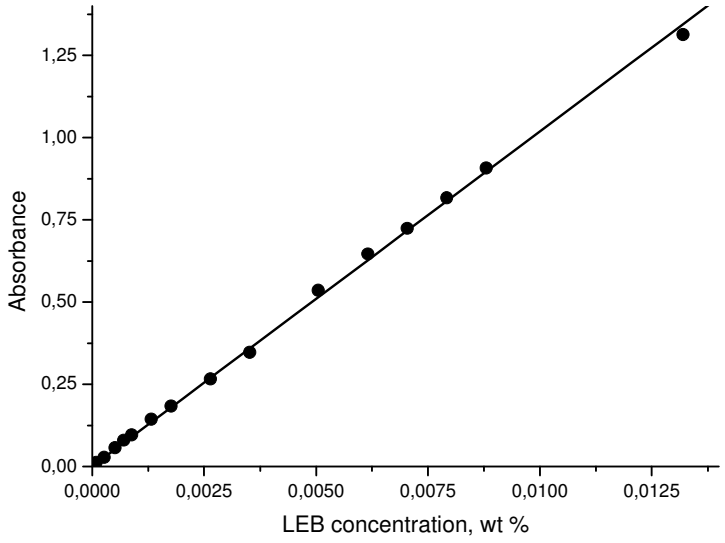

Fig. S2. Concentration dependence of the absorbance of reduced PANI in solution NMR at a wavelength of 343 nm.

Knowing C_s and initial quantity of the dedoped composite taken for the analysis, we calculate the content of dedoped PANI in this composite using simple calculation, which for convenience can be expressed by the equation

$$C\ [wt\ \%] = (V \cdot \rho + m_1 + m_2)C_s/m_1,$$

where V [cm^3] is the total volume of NMP, ρ [g/cm^3] is the density of NMP, m_1 [g] is the mass of dedoped powder composites used for making of solution, m_2 [g] is the mass of ascorbic acid, and C_s [wt %] is the concentration of PANI in solution of PC/PANI composites with ascorbic acid in NMP.

If the NMP volume and the weight of the PC/PANI composite and ascorbic acid are as above, the content of dedoped PANI in PC/PANI composites is calculated as $C = 634.1 \cdot C_s$.

The dedoped PANI content in the composite under the study can be easily recalculated for the doped PANI one in the form of the salt $PANI(TSA)_{0.5}$, i.e. for the stoichiometric ratio of the acid-dopant and the imine nitrogens of PANI.

2. The Size Exclusion Chromatography (SEC) approach to determine molecular weight characteristics of PANI in the PANI/PC composite

SEC was applied to the joint solution of LEB and PC (see part 2.4 of the paper) being eventually the binary polymer mixture. It is known that molecular weight characteristics of components of binary polymer mixtures can be characterized simultaneously without physical separation by SEC method equipped with multiple detectors [3, 4]. The individual peaks of the two components are separated from the overlapped chromatogram by simultaneously solving the response signal intensities from two concentration detectors. This complicated procedure results if determining molecular weight characteristics of the both components [3, 4]. A much simpler situation is if there is an interest in the characteristics of solely one polymer from the mixture. In this case there can be used one selective detector. Based on this understanding and on the fact that we did not need characteristics of PC we adjusted the known multiple detection approach [3,4] for a detection of solely PANI with one ultraviolet (UV) detector which can be easily tuned to a necessary UV wavelength.

This simplified approach stems from the fact that these polymers absorb in different spectral ranges (Fig.S1) and UV detecting allows to discriminate the PANI from PC. Namely, UV detector, tuned for the LE (reduced PANI) spectral wavelength 343 nm, registers only macromolecules of this polymer (Fig. S3). PC macromolecules do not absorb under this condition and UV detector does not see them. This means that due to the strong spectral difference between the PANI and PC and using only UV detector, we can simply ignore the presence of PC macromolecules under investigation conditions and measure the high molecular weight of solely one component (PANI) of the binary polymer mixture.

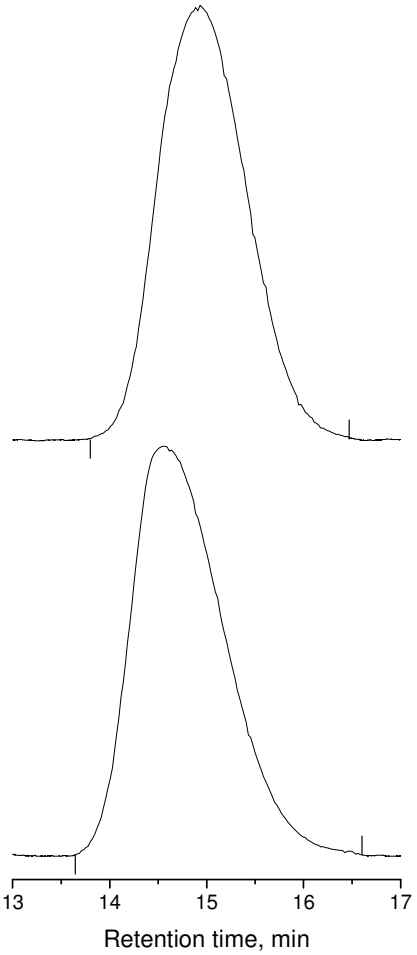

Fig. S3. SEC chromatograms for the net PANI (top) and PANI from the composite (bottom).

References

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