Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

Development and characterisation of switchable polyaniline-functionalised flow-through capillary monoliths

Patrick Floris[I], Damian Connolly[II] , Blanaid White[I] and Aoife Morrin [I]*

[I] School of Chemical Sciences, National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland.

[II] Pharmaceutical and Molecular Biotechnology Research Centre (PMBRC), Department of Chemical and Life Sciences, Waterford Institute of Technology, Waterford, Ireland.
** Tel: +353 1 700 6730; Fax: +353 1 700 5503; E-mail: aoife.morrin@dcu.ie*

1. Materials and methods

1.1 Fabrication of polymer monoliths

Deoxygenated monomer mixtures were pumped into fused silica capillary (250 µm x 100 mm) which had been vinylised using a previously described procedure [1]. All monoliths were thermally polymerised for 24 hr at 70 °C with the exception of the PS-*co*-DVB monoliths which were polymerised for 24 hr at 80 °C followed by a final rinse in methanol at 1 µL/min for 3 hr to remove porogens and unreacted monomers. A schematic illustrating the monomers and cross-linkers used for the preparation of polymer monoliths is shown in Figure ESI-1.

1.2 Evaluation of axial homogeneity of PANI coatings using sC^{4}D

Each monolith was first equilibrated with 1 m*M* HNO_3 at 3 µL/min for 6 hr followed by continuous flushing of this solution during subsequent sC^{4}D profiling steps. The C^{4}D detector head was manually moved along the length of the monolith at 5 mm increments while recording the conductive response at each measurement location. To connect the capillary monolith to the pumping apparatus a micro-tight union and PEEK sleeve was required which covered the first 2 cm of the column, therefore throughout this experiment the first 2 cm remained uncharacterised. For all monoliths the detector conditions were; frequency: 2x high, offset: 000, and input voltage: -30 dB (with the exception of the AEMA-*co*-EDMA monolith for which the input voltage setting was -24 dB).

1.3 Determination of ion-exchange capacity of PANI-coated monoliths

A PS-*co*-DVB monolith, which was modified 3 times with PANI, was used to evaluate the ion-exchange properties of the stationary phase. The ion-exchange capacity was calculated using a bromide adsorption/desorption method where the column was filled initially with a 20 m*M* bromide solution for 30 min at 5 µL/min, rinsed with water for another 30 min and flushed with 10 m*M* perchlorate at the same flow rate to elute the bound bromide which was detected using UV detection at 210 nm (Figure ESI-3-a). The column volume was also determined by flushing deionised water for 30 minutes at 5 µL/min followed by 10 m*M* perchlorate at the same flow-rate (Figure ESI-3-b).

NOTE: Bromide was initially selected as an anion to evaluate the anion-exchange capacity of the PANI-modified PS monolith on account of a previously described procedure reported by Hutchinson *et al.* [2] (). This anion however was not sufficiently retained under the chromatographic conditions used. According to the order of retention of monovalent anions, iodide is more strongly retained than bromide and hence iodide was selected for to demonstrate the ion-exchange properties of the prepared stationary phases.

1.4 IR characterisation of PANI-modified PS monoliths

Infra-red spectra were obtained on PS monoliths modified with PANI in both doped and dedoped state. Characteristic bands for PS were visualised in both monoliths between 1600 and 1492 cm^{-1} (typical of aromatic ring vibrations) and also between 2900-3000 cm^{-1} indicative of C-H vibrations (aliphatic and aromatic). Peaks at 1300 cm^{-1} and 1450 cm^{-1} for C-N and C-C stretching in PANI were also present. In particular, the presence of a band at 1142 cm^{-1} was attributed to protonated imine quinoid N, which is characteristic of the doped form of PANI.

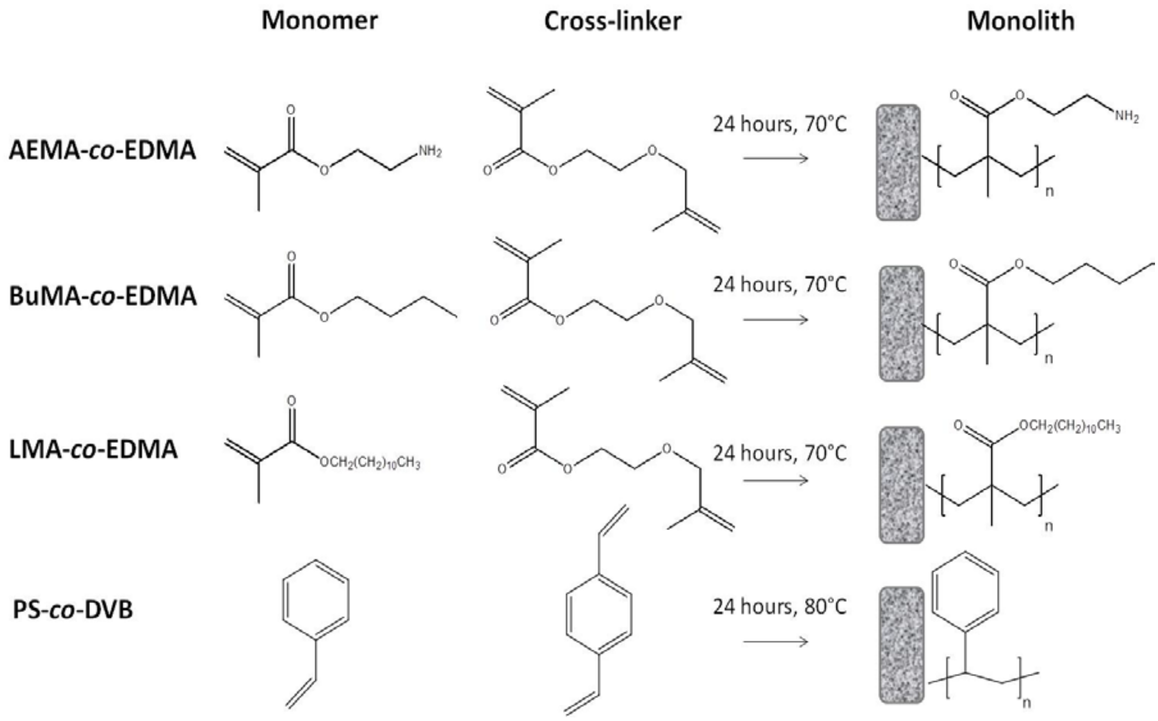

Figure ESI-1: Schematic showing the structures of monomers and cross-linkers used for the preparation of polymer monoliths.

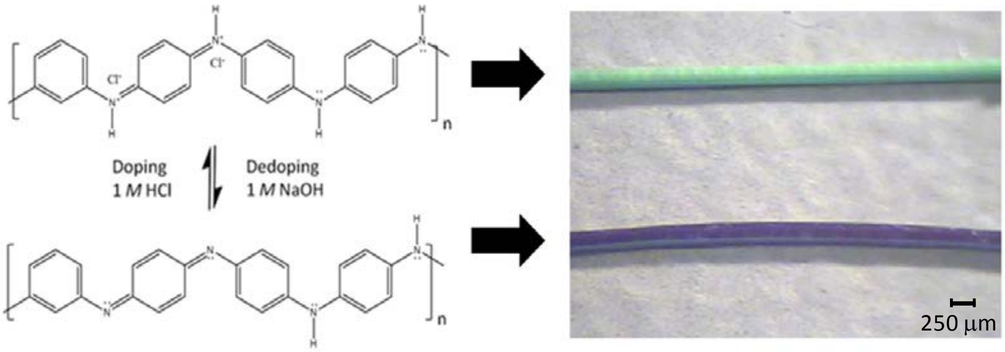

Figure ESI-2: Schematic showing the reversible doping/dedoping mechanism of PANI. A colour digital photograph of a PANI-coated PS-*co*-DVB monolith in the doped and de-doped state is also included (right).

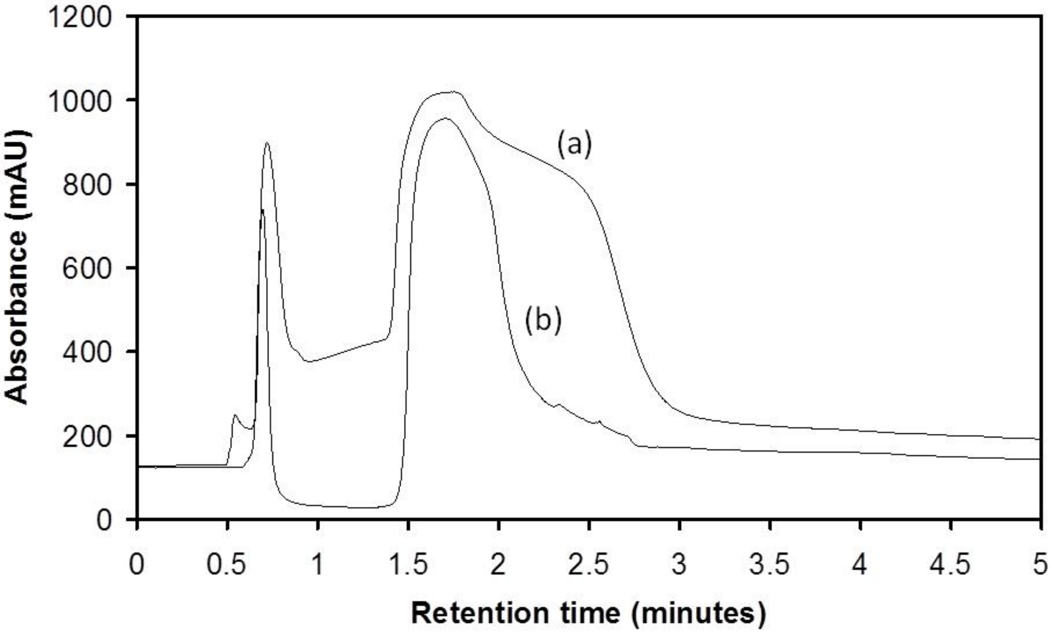

Figure ESI-3: Determination of ion-exchange capacity of a PANI-modified PS monolith (a) filled with 20 mM Br and (b) deionised water. Eluent: 10 mM perchlorate. Flow-rate: 5 μL/min. Detection: UV at 210 nm.

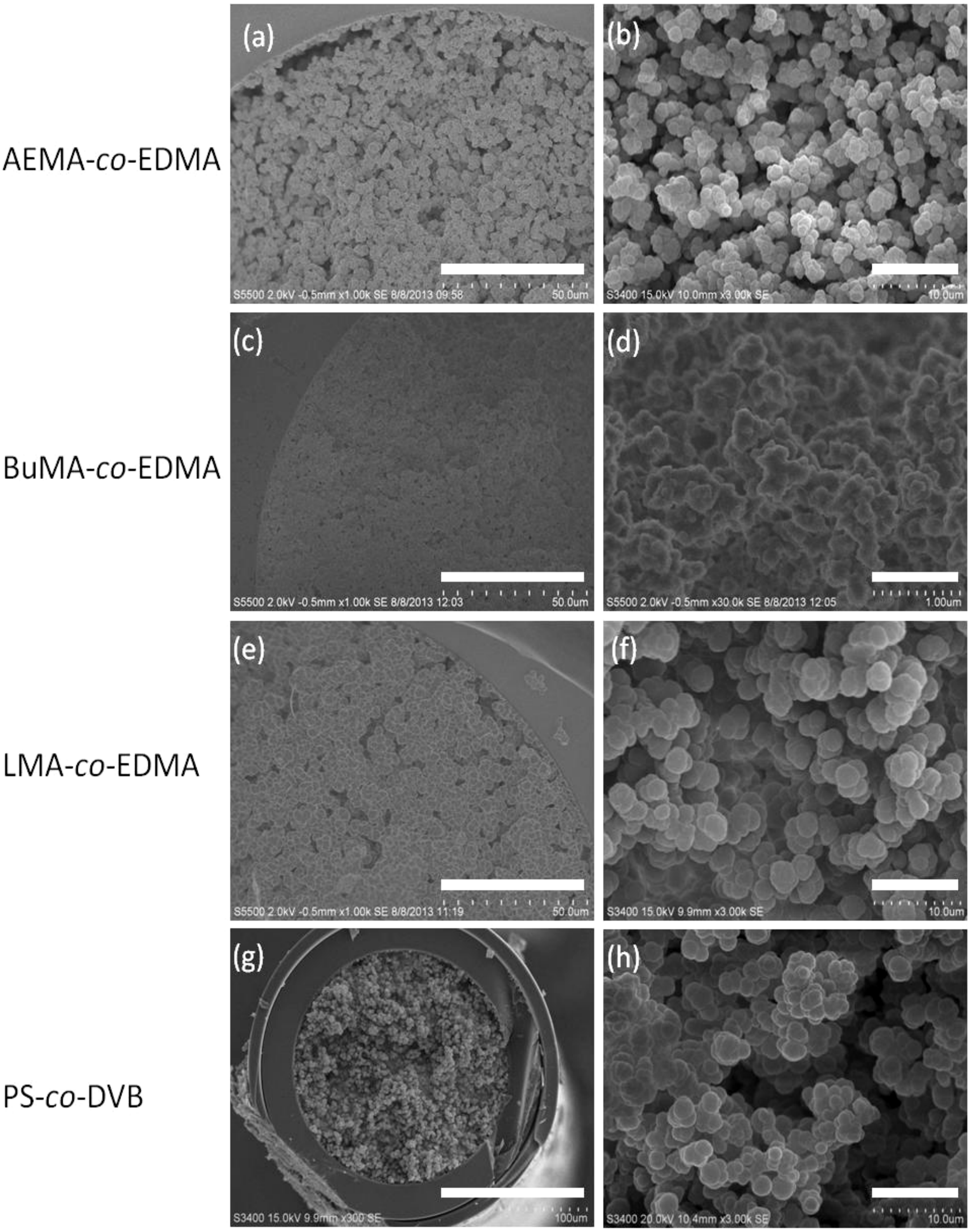

Figure ESI-4: FE-SEM images illustrating the macro-porous structure of (a,b) AEMA-*co*-EDMA, (c,d) BuMA-*co*-EDMA, (e,f) LMA-*co*-EDMA and (g,h) PS-*co*-DVB polymer monoliths (various magnifications).

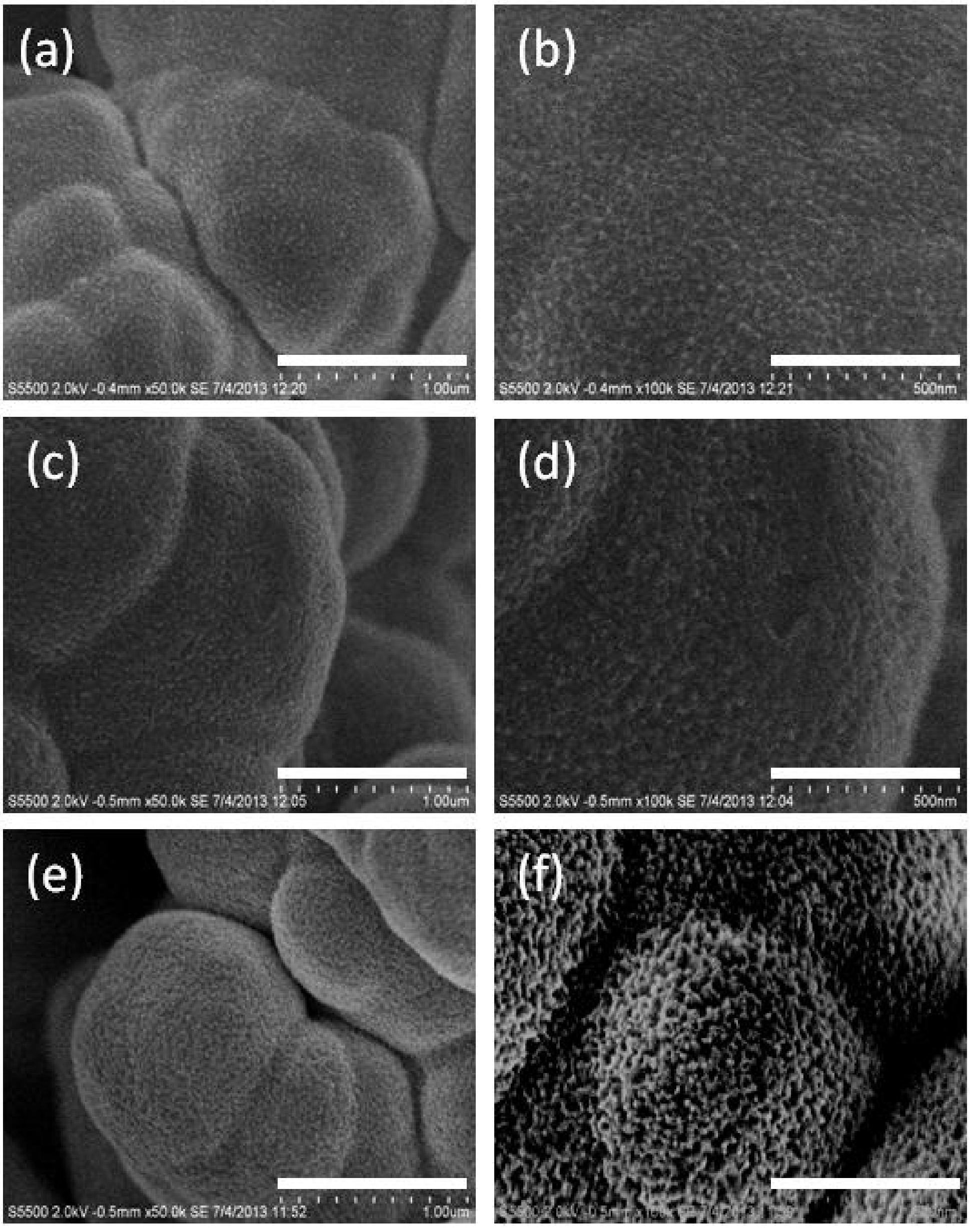

Figure ESI-5: FE-SEM images of: (a,b) a blank PS-*co*-DVB monolith after a first modification with PANI, (c,d) after a second and (e,f) after a third modification step (magnification: 50,000x and 100,000x).

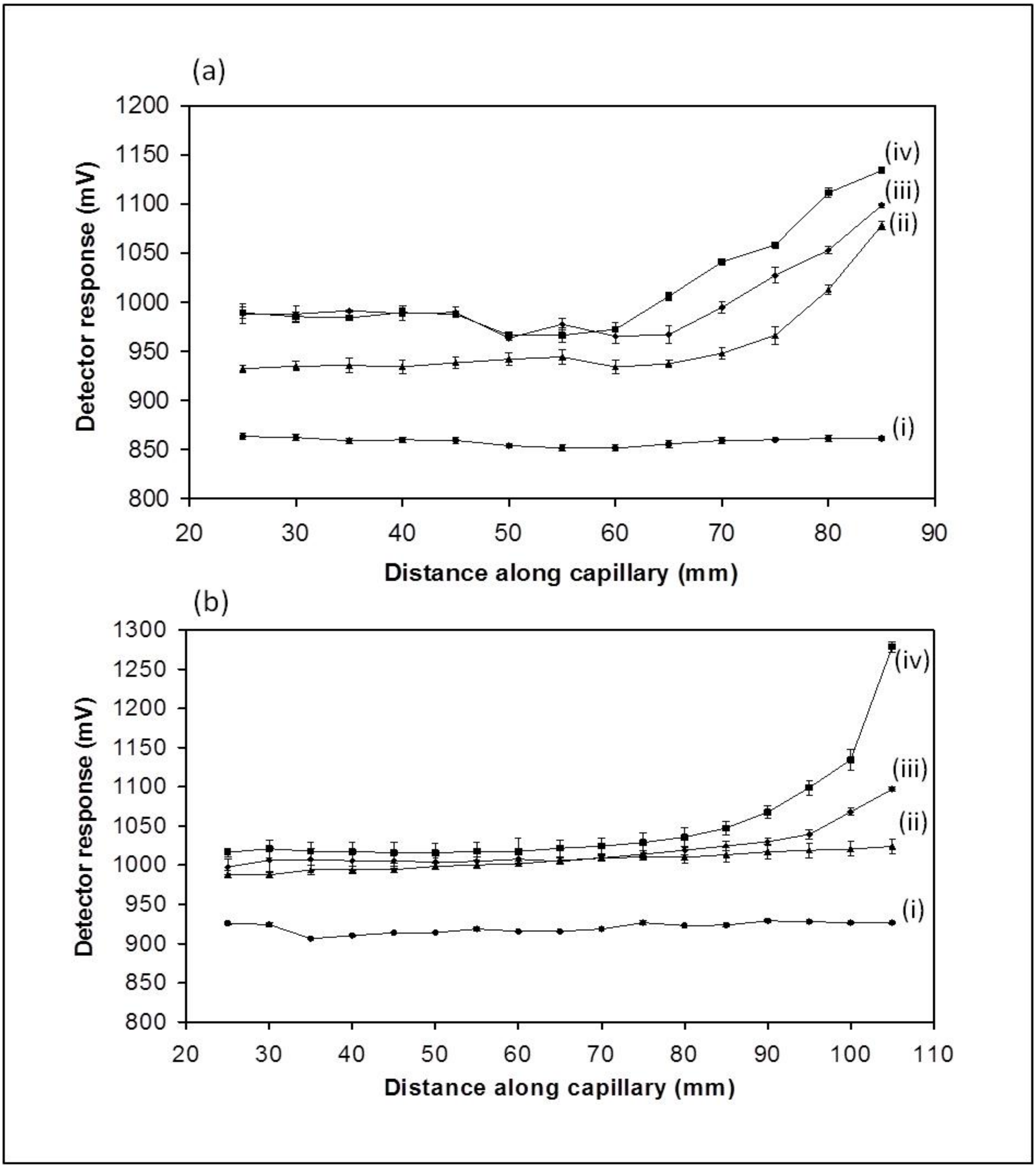

Figure ESI-6: sC^{4}D profiles of a second (a) and third (b) PS-*co*-DVB monolith subjected to three individual PANI coating steps each. Scanning conditions are as described for Figure 2.

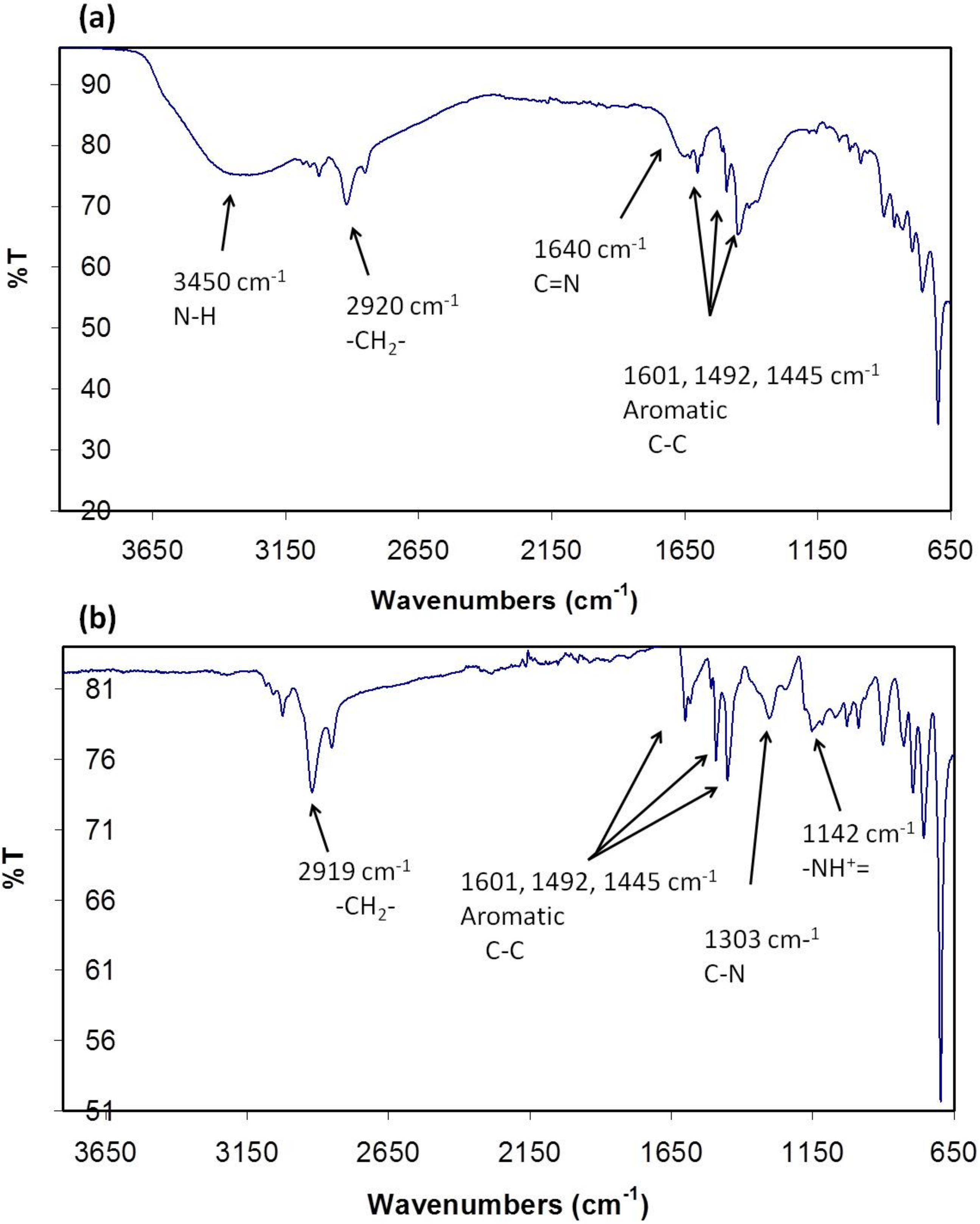

Figure ESI-7: IR-spectra of (a) dedoped and (b) doped PANI-modified PS-*co*-DVB polymer monoliths.

[1] Connolly, D., O’Shea, V., Clarke, P., O’Connor, B., Paull, B., J. Sep. Sci., 2007, 30, 3060–3068.

[2] Hutchinson , J.P., Hilder, E.F., Shellie, R.A. Smith, J.A., Haddad, P.R., Analyst, 2006, **131**, 215-221.