

Electronic Supplementary Information (ESI) for:

**Well-defined polyvinylpyridine-*block*-polystyrene diblock copolymers *via* RAFT aqueous-alcoholic dispersion polymerization: Synthesis and isoporous thin film morphology**

Katharina Nieswandt,<sup>a</sup> Prokopios Georgopoulos<sup>a, \*</sup> and Volker Abetz<sup>a,b, \*</sup>

<sup>a</sup> *Helmholtz-Zentrum Geesthacht, Institute of Membrane Research, Max-Planck-Straße 1, 21502 Geesthacht, Germany.*

<sup>b</sup> *Institute of Physical Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany*

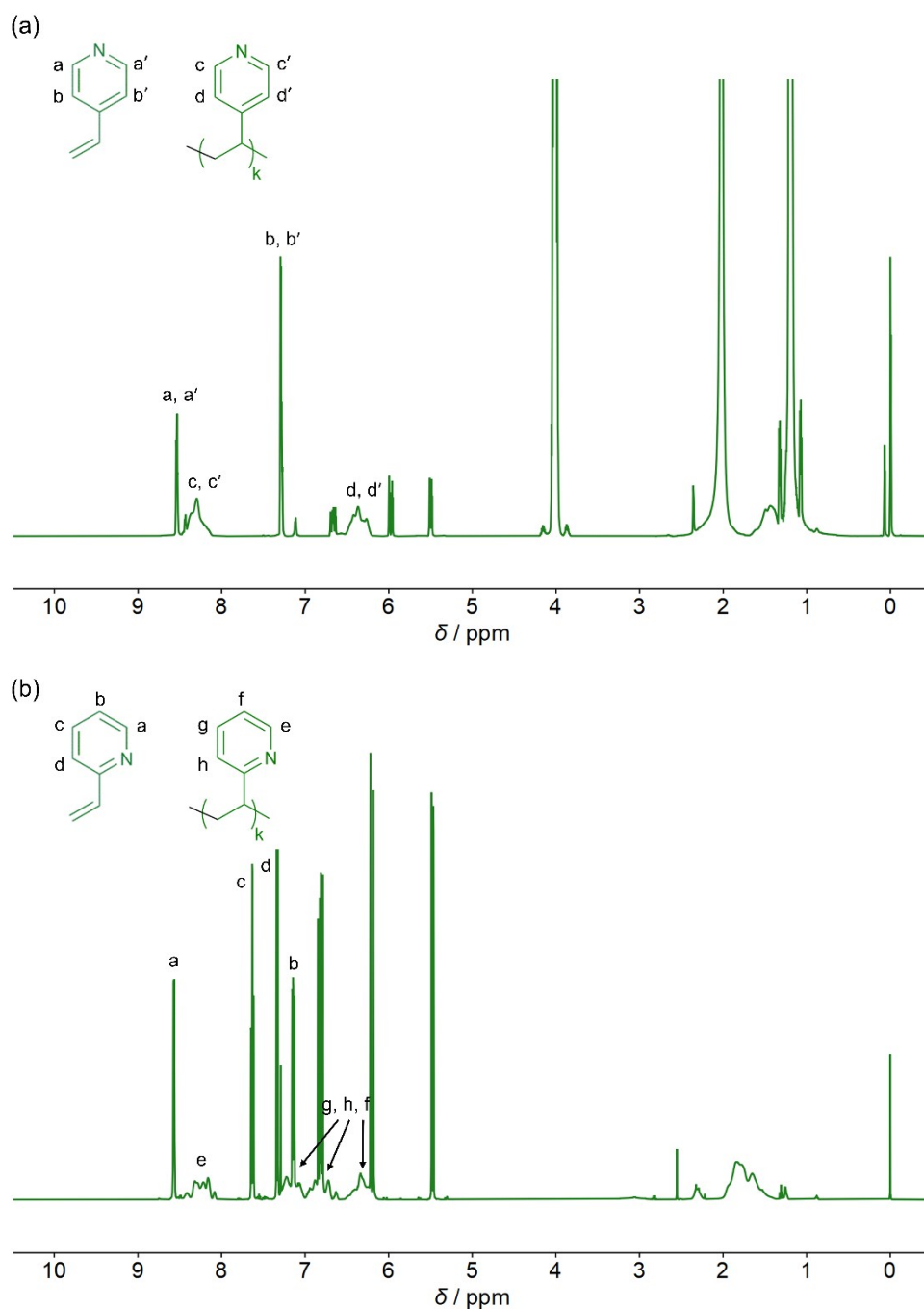
*E-Mail: [prokopios.georgopoulos@hzg.de](mailto:prokopios.georgopoulos@hzg.de), [volker.abetz@hzg.de](mailto:volker.abetz@hzg.de)*

**ORCID iD**

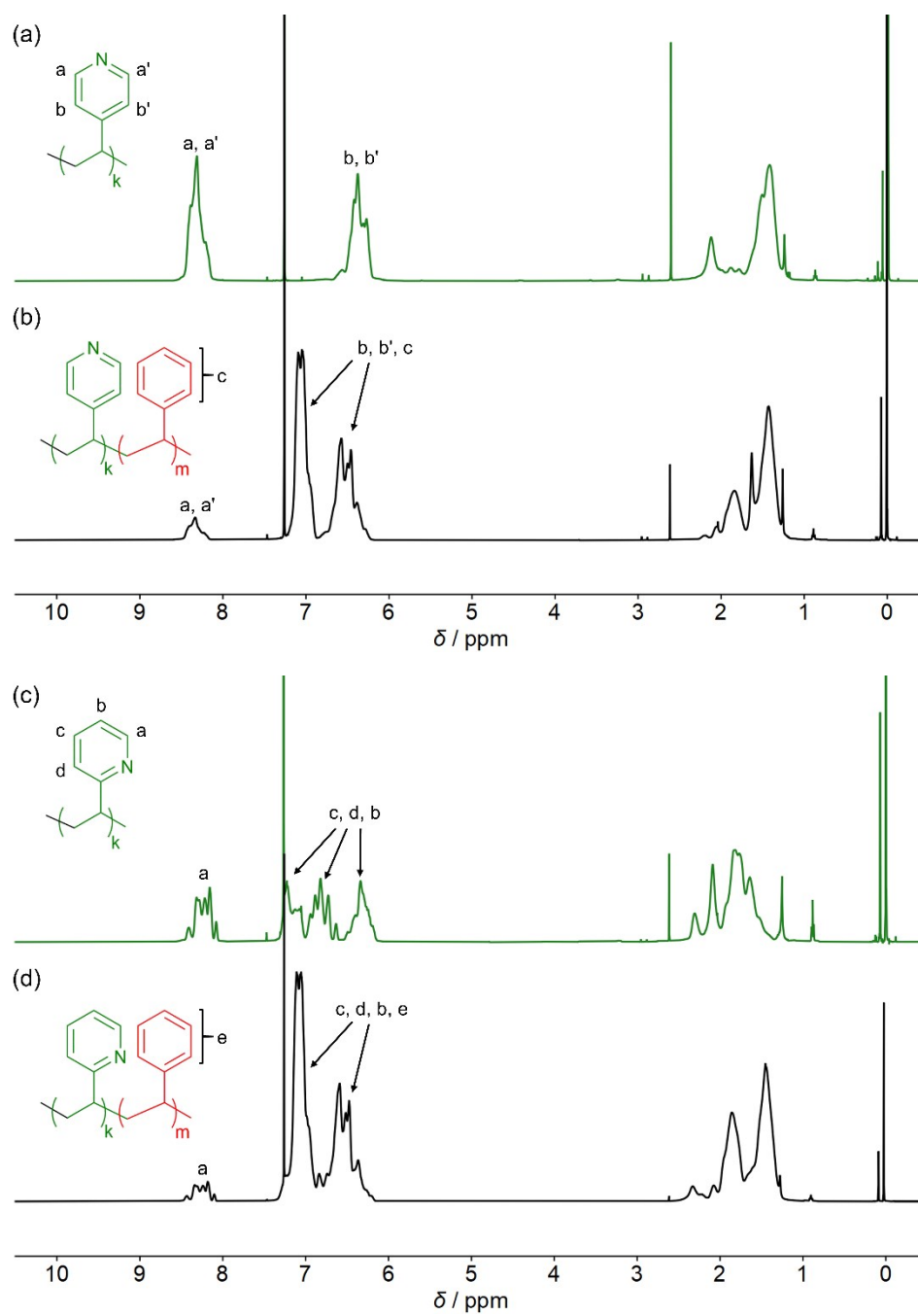
Katharina Nieswandt: 0000-0001-7454-1908

Prokopios Georgopoulos: 0000-0002-6394-0628

Volker Abetz: 0000-0002-4840-6611



**Figure S 1.**  $^1\text{H}$ -NMR spectra recorded in  $\text{CDCl}_3$  of a typical reaction mixture (a) for 4VP polymerization; (b) for 2VP polymerization. All relevant protons of 4VP, P4VP, 2VP and P2VP are assigned to the respective signals. The conversion of 4VP was determined from the integral ratio of the aromatic P4VP signal at 8.48-8.09 ppm ( $c, c'$ ) and the monomer signal at 8.55 ppm ( $a, a'$ ). The conversion of 2VP was determined from the integral ratio of the aromatic P2VP signal at 8.47-8.02 ppm ( $e$ ) and the monomer signal at 8.57 ppm ( $a$ ).

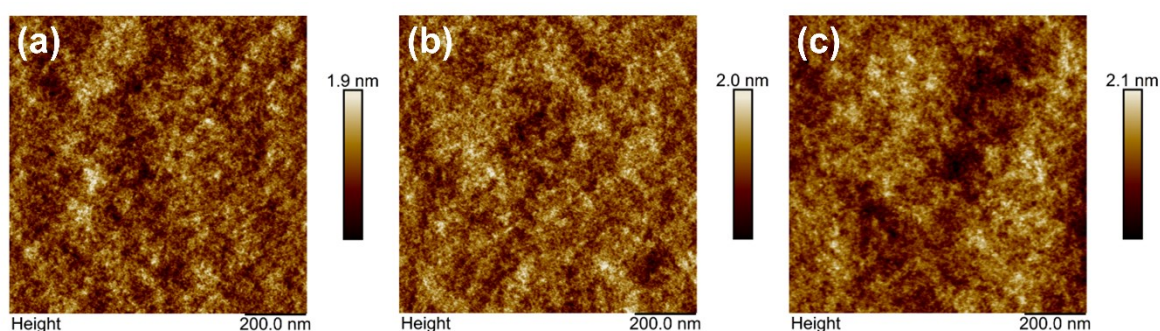
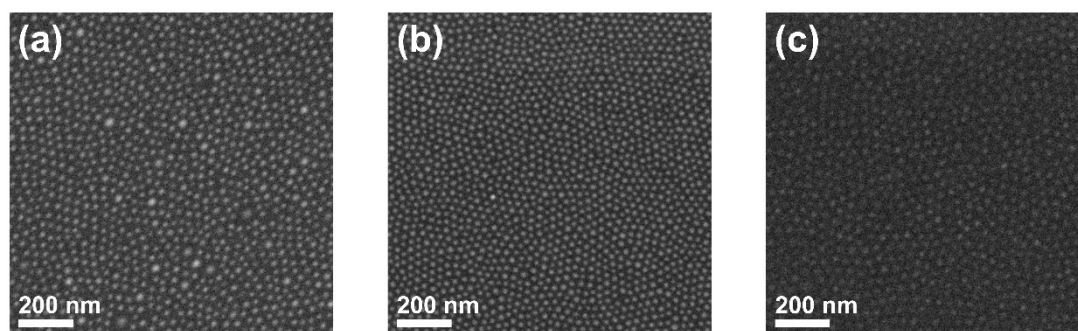


**Figure S 2.**  $^1\text{H-NMR}$  spectra recorded in  $\text{CDCl}_3$  for (a) P4VP<sup>20</sup> macroRAFT agent; (b) P4VP<sub>17</sub>-PS<sub>83</sub><sup>119</sup> diblock copolymer; (c) P2VP<sup>20</sup> macroRAFT agent and (d) P2VP<sub>24</sub>-PS<sub>76</sub><sup>93</sup> diblock copolymer.

**Table S 1.** Hansen solubility parameters for styrene, methanol and water.<sup>1</sup>

Solvent	$\delta_D$ [MPa <sup>1/2</sup> ] <sub>a</sub>	$\delta_P$ [MPa <sup>1/2</sup> ] <sub>b</sub>	$\delta_H$ [MPa <sup>1/2</sup> ] <sub>c</sub>	$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2}$ [MPa <sup>1/2</sup> ] <sub>d</sub>
Styrene	18.6	1.0	4.1	19.1
Methanol	15.1	12.3	22.3	29.6
Water	15.5	16.0	42.3	47.8

<sup>a, b, c, d</sup> Dispersion solubility parameter  $\delta_D$ , polar solubility parameter  $\delta_P$  and hydrogen bonding solubility parameter  $\delta_H$ . The Hansen three dimensional solubility parameter  $\delta$  is given by the equation  $\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2}$ .

**Figure S 3.** Spin-coated thin film of a 2 wt % PVP-*b*-PS chloroform solution after thermal annealing at  $T_{\text{annealing}} = 180$  °C. Surface topography *via* QNM AFM height images (1  $\mu\text{m} \times 1 \mu\text{m}$ ); (a) P4VP<sub>186</sub>-PS<sub>851</sub> diblock copolymer; (b) P4VP<sub>168</sub>-PS<sub>672</sub> diblock copolymer; (c) P2VP<sub>215</sub>-PS<sub>672</sub> diblock copolymer.**Figure S 4.** SEM images (EsB detector) of spin-coated thin film of a 2 wt % PVP-*b*-PS chloroform solution after thermal annealing at  $T_{\text{annealing}} = 180$  °C. To obtain a better contrast between the microphases, P4VP and P2VP were selectively stained in I<sub>2</sub>-vapor for 15 min; (a) P4VP<sub>186</sub>-PS<sub>851</sub> diblock copolymer; (b) P4VP<sub>168</sub>-PS<sub>672</sub> diblock copolymer; (c) P2VP<sub>215</sub>-PS<sub>672</sub> diblock copolymer.

## References

1. C. M. Hansen, *Hansen solubility parameters: a user's handbook*, CRC press, 2002.