Electronic Supplemental Information

Swelling Behavior of Bisensitive IPNs for Microfluidic Applications

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ATR-FTIR measurements

ATR spectra of freeze-dried samples were collected using FTIR-spectrometer Vertex 80v (Bruker) equipped with a Golden Gate Diamond ATR unit (SPECAC) and a MCT-detector. The used spectroscopic range was 4000-600 cm^{-1}. The spectral resolution was 4 cm^{-1} and 100 scans were co-added for every spectrum. To compare ATR spectra properly, baseline correction and normalization were applied to all spectra. The combined methyl and methylene band area was used as reference in each spectrum.

The calibration curve was based on normalized spectra of an adequate mixture of PN*i*PAAm, PAA and PAAm. Areas of amide II band of PN*i*PAAm at 1535 cm^{-1} were calculated and plotted as a concentration function.

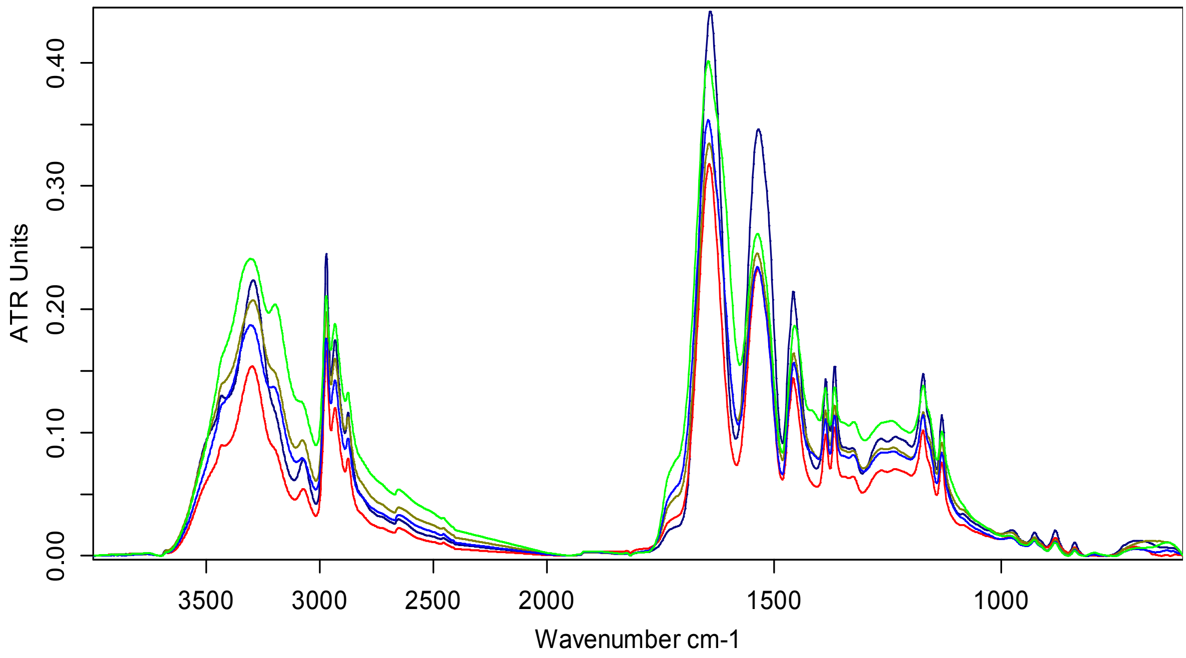

Figure 1: Spectra of PNiPAAm, PAA and PAAm mixtures for the calibration.

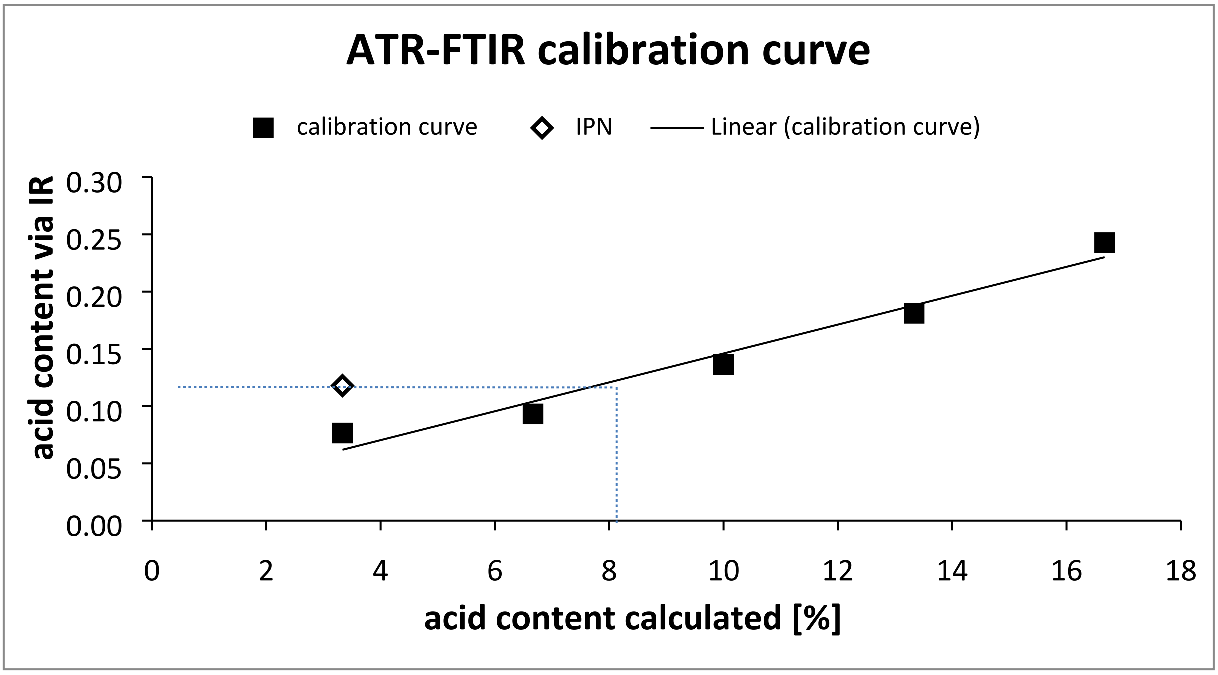

Figure 2: Calibration curve with sample signal.

Figure 3: Raw data of calibration curve and the investigated IPN sample.

PNIPAAm content	CH_2/CH_3-reference [area]	C=O of acid [area]	NPIAAm [area]	NIPAAm content	acid content	acid calculated [%]
50%	0.0395	0.00959	0.05592	1.42	0.24	16.67
60%	0.04059	0.00735	0.05262	1.30	0.18	13.33
70%	0.04518	0.00616	0.05723	1.27	0.14	10.00
80%	0.04625	0.00431	0.05187	1.12	0.09	6.67
90%	0.07058	0.0054	0.08248	1.17	0.08	3.33
sample	0.08572	0.01011	0.11938	1.39	0.12	3.33

Derivation of the form correction factor

It is not trivial to get proper values of the cooperative diffusion coefficient D_{coop} from common samples. The described formula in the literature is only useful for extreme cases like very long or flat cylinders or spheres. The investigated samples were of cylindrical shape with an aspect ratio (AR) around 1. This leads to the necessity of a correction factor. Otherwise the calculated values for D_{coop} would be too small.

The approach is the assumption of the constancy of the ratio of the cooperative diffusion coefficient and the volume specific surface for all samples. The correction factor f is defined to be the ratio of the cooperative diffusion coefficient of a sample and a sphere or of the corresponding volume specific surfaces, respectively.

$$\frac{D_{coop,\,cylinder}}{A_{v,\,cylinder}} = \frac{D_{coop,\,sphere}}{A_{v,\,sphere}}$$

$$\frac{A_{v,\,cylinder}}{A_{v,\,sphere}} = f = \frac{D_{coop,\,cylinder}}{D_{coop,\,sphere}}$$

$$D_{coop,\,cylinder} = f \cdot D_{coop,\,sphere}$$

This leads to following volume-specific surface areas of common special, disc-like and worm-like samples

$$A_{v,sphere} = \frac{\pi d^2}{\frac{1}{6}\pi d^3} = \frac{6}{d} \qquad f = \frac{A_{v,\,cylinder}}{A_{v,\,sphere}} \qquad D_{exp} = \frac{3}{3} D_{coop}$$

$$A_{v,worm} = \frac{\pi d h}{\frac{\pi}{4} d^2 h} = \frac{4}{d} \qquad f_{worm} = \frac{2}{3} \qquad D_{exp} = \frac{2}{3} D_{coop}$$

$$A_{v,disc} = \frac{2\frac{\pi}{4} d^2}{\frac{\pi}{4} d^2 h} = \frac{2}{h} \qquad f_{disc} = \frac{1}{3} \qquad D_{exp} = \frac{1}{3} D_{coop}$$

The general equation for the volume-specific surface area of cylindrical samples:

$$A_{v,cylinder} = \frac{2\frac{\pi}{4}d^2 + \pi dh}{\frac{\pi}{4}d^2 h} = \frac{2d + 4h}{dh}$$

$$f = \frac{2d + 4h}{dh} \cdot \frac{d}{6} = \left(\frac{2}{h} + \frac{4}{d}\right)\frac{d}{6}$$

In extreme cases they give the same ratio of the measured D_{coop} compared with DLS measurements like the literature (1/3 for flat discs and 2/3 for worm-like cylinders and 3/3 for spherical samples).

The shape correction factor can be specified for flat and long cylinders in order to further simplify the equation:

$$f(AR)_{h>d} = \left(\frac{2}{AR} + \frac{4}{1}\right)\frac{1}{6} = \frac{1 + 2AR}{3AR}$$

$$f(AR)_{d>h} = \left(\frac{2}{1} + \frac{4}{AR}\right)\frac{1}{6} = \frac{AR + 2}{3AR}$$

This correction factor allows for investigating cylindrical samples of arbitrary aspect ratios, correct the calculated cooperative diffusion coefficients from the swelling kinetics and compare them with the results from DLS measurements.

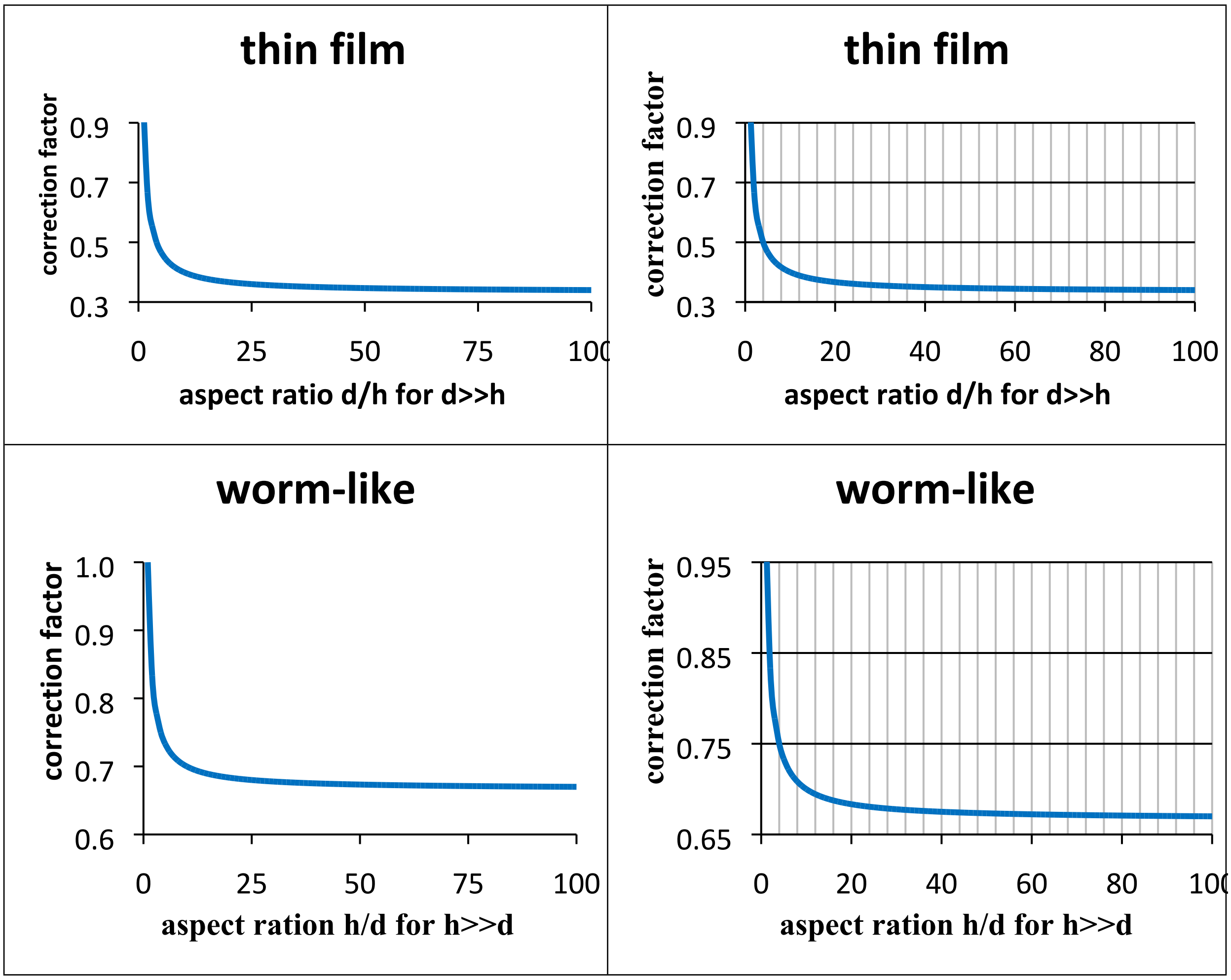

Figure 4: Graphical description of the form correction factor for flat (top) and long (bottom) cylindrical samples.