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Supporting Information

for

Self-Assembled Monolayers of Dendritic Polyglycerol Derivatives on Gold that Resist the Adsorption of Proteins

By

*Conrad Siegers[a], Markus Biesalski[c], and Rainer Haag[a,b],**

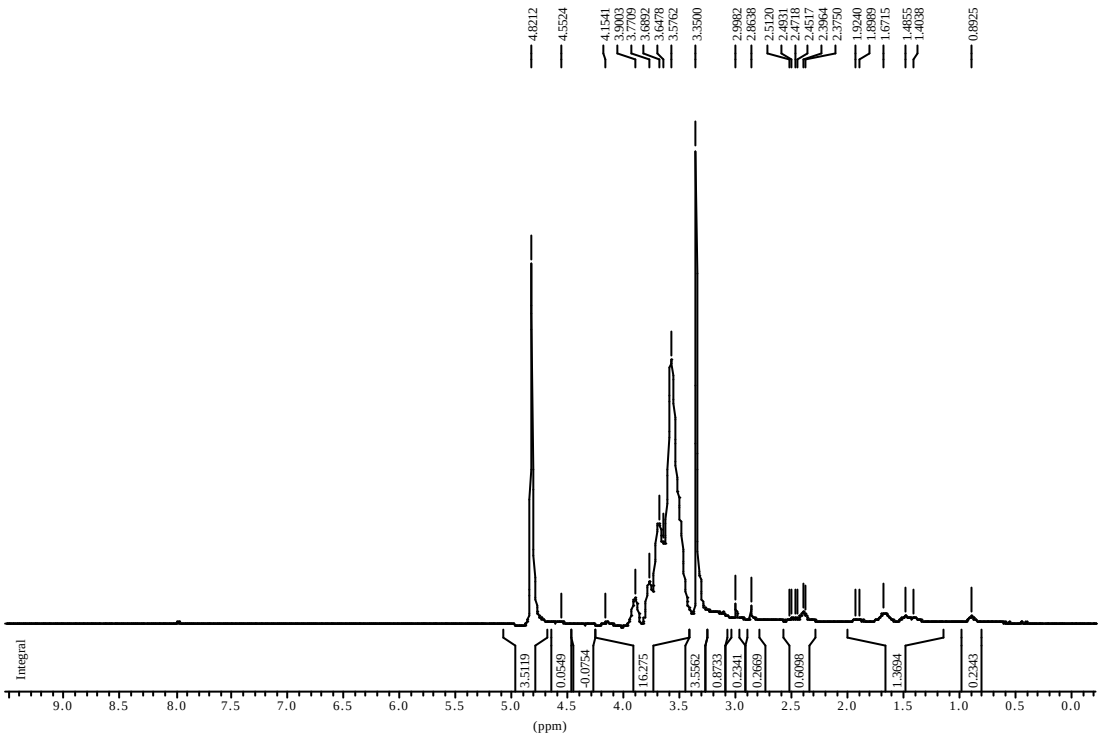
[a] Prof. Dr. R. Haag, Dipl.-Chem. C. Siegers, Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Str. 21, 79104 Freiburg.

[b] **New Address**: Organische Polymerchemie, Universität Dortmund, Otto-Hahn-Str. 6, 44227 Dortmund, Germany. Email-Adresse: haag@chemie.uni-dortmund.de; Internet: www.polytree.de, Fax: +49-231-755 6148.

[c] Dr. M. Biesalski, Institut für Mikrosystemtechnik (IMTEK), Universität Freiburg, Georges-Köhler-Allee 103, 79110 Freiburg, Germany

Contents

^{1}H-NMR, PG_{5000}-Thioc/TMP **5**:



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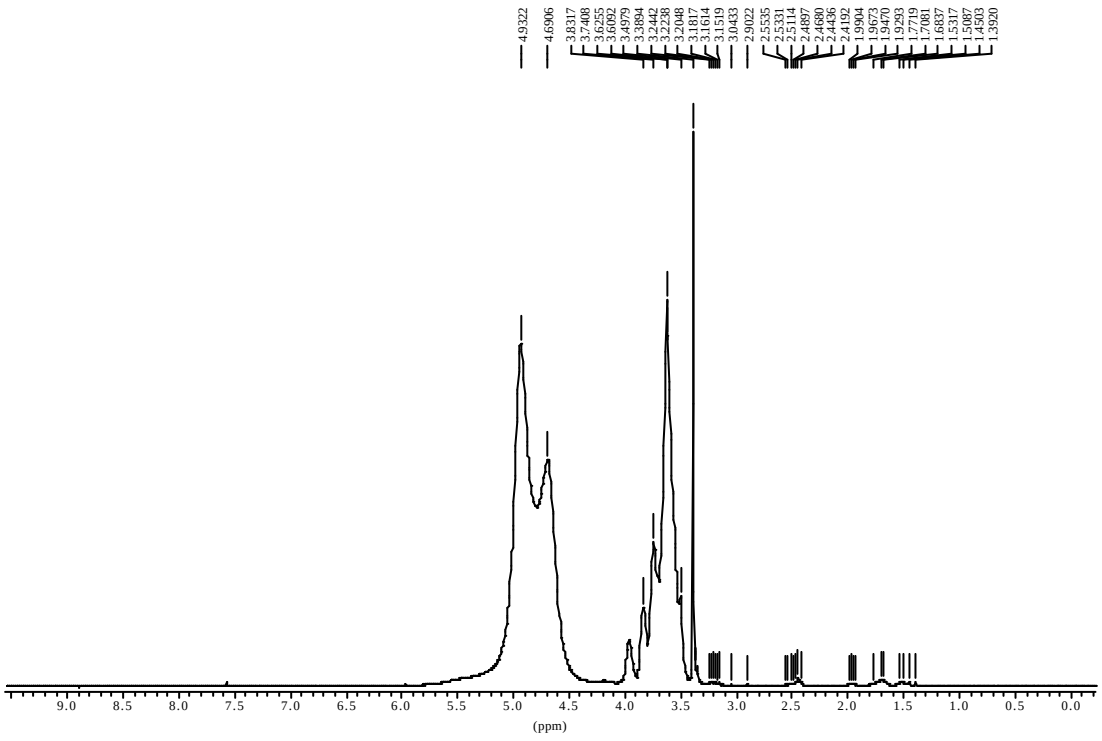

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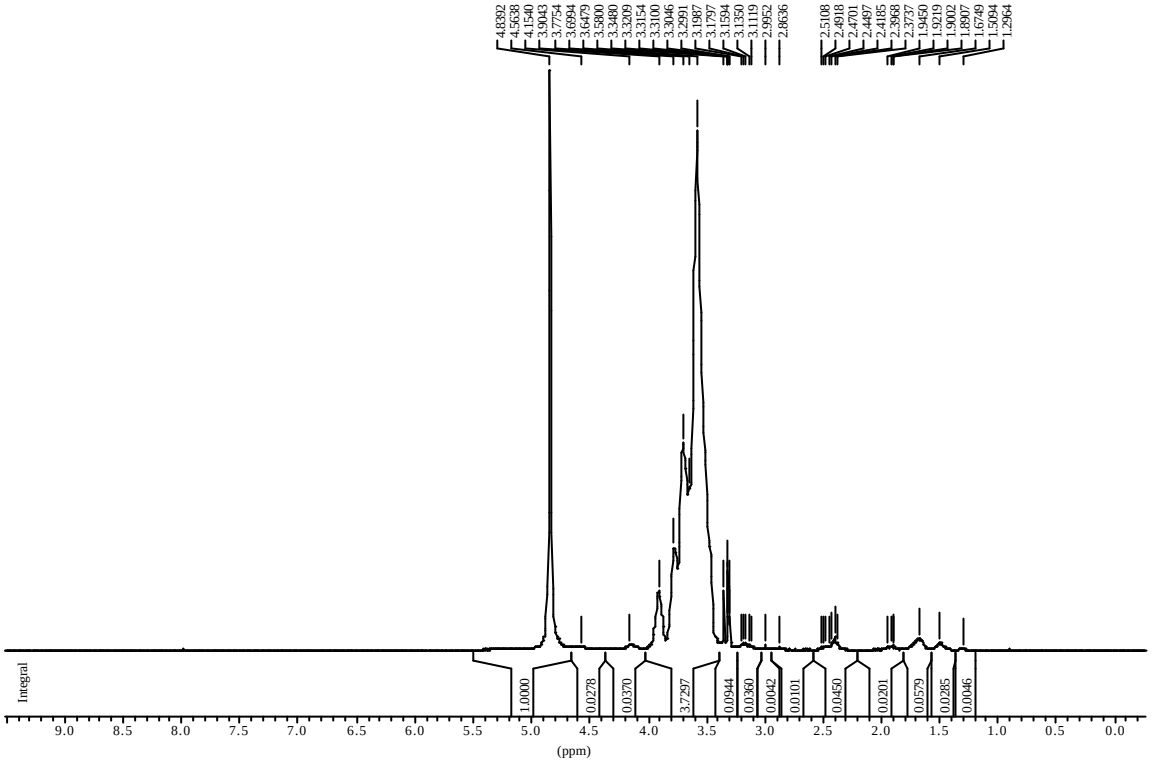

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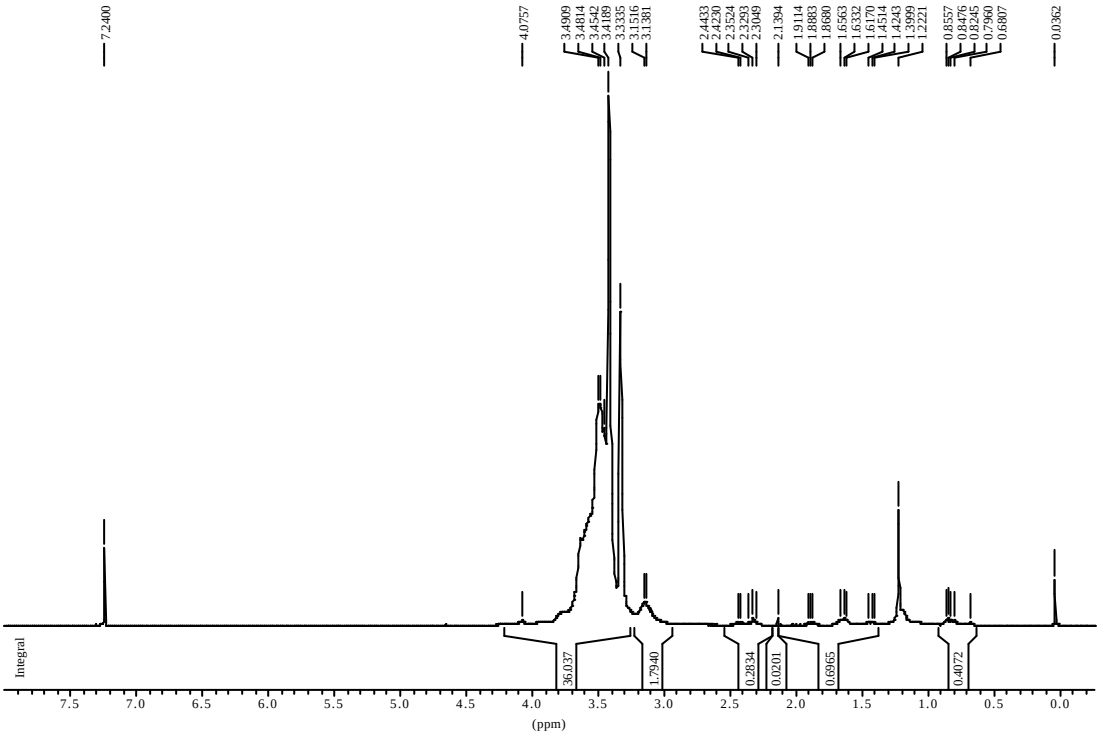

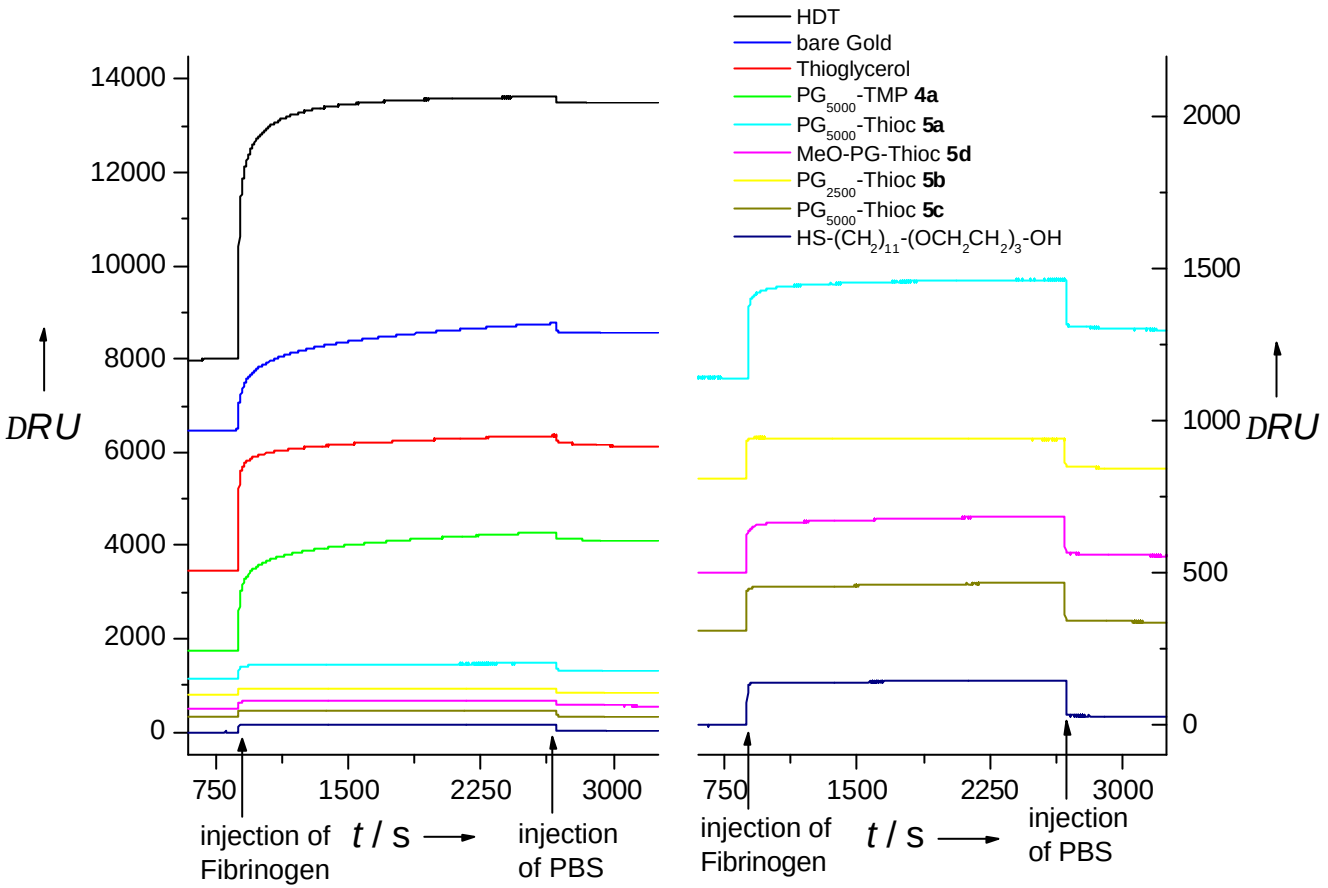

Figure 1. SPR-sensograms of fibrinogen adsorption to PG-SAMs recorded according to the procedure described in the article using the Biacore-Upgrade SPR-device.

Results of the characterization of SAM-formation measured with a self-made SPR-spectrometer, which allows manual sample injection via a syringe and which admits to apply a broader range of experimental conditions as opposed to the Biacore-Upgrade device used in protein adsorption studies. In the former set-up, the change in reflectivity is monitored at a constant angle. The incident laser light had a wavelength of l = 623.8 nm. The reflected light intensity is measured as a voltage generated from a measuring amplifier to which a photodiode is connected; thus the unit in which the reflectivity R (R = intensity of incident light / intensity of reflected light) is reported here is mV. The sensogram below show the adsorption behaviour of PG_{5000}-Thioc **5c** in MeOH (Figure 2) to a semitransparent gold film supported on LaSFN9-glass.

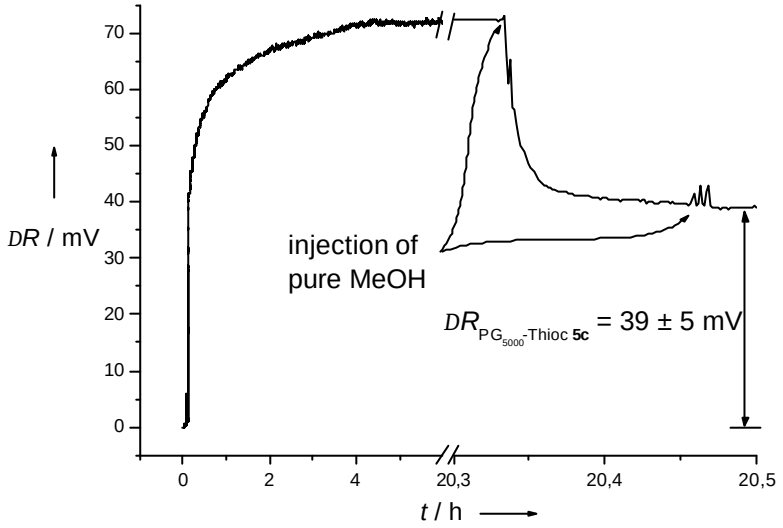

Figure 2. Sensogram of the adsorption of PG_{5000}-Thioc **5c** in MeOH to a gold surface. After the injection of the PG solution at t = 0 h a monotone increase in DR is observed over a period of 4 hours after which a plateau level is reached. This indicates, that a full monolayer has been formed. After rinsing the surface with pure MeOH (the points in time at which pure MeOH was injected are indicated by arrows), the reflectivity decreases, and a DR-value of 39 ± 5 mV ($DR_{PG} = R_{\text{after exposure to PG}} - R_{\text{before exposure to PG}}$) points to the formation of a full, stable PG-monolayer.

Calculation of PG layer thickness for PG_{5000}-Thioc 5c in MeOH. In order to calculate the layer thickness of the swollen PG_{5000}-Thioc-SAM, a semitransparent gold substrate supported on LaSFN9 glass was mounted onto the SPR-spectrometer. From this substrate an SPR-spectrum was recorded with air and MeOH in the measuring cell (Figure 3a and b, respectively). These spectra were used to fit the parameters summarized in Table 1 to the experimental data.

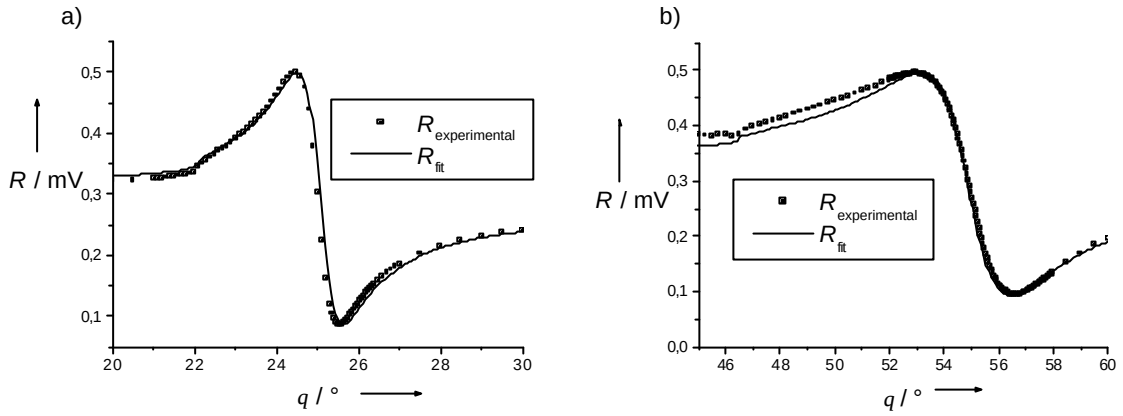

Figure 3. SPR-spectrum of the semitransparent gold substrate a) towards air and b) towards MeOH used in the adsorption experiment shown in Figure 2.

Table 1. Parameters used for the fitting of SPR-spectrum of the semitransparent gold substrate used in the adsorption experiment shown in Figure 2. e' and e'' are the real and imaginary part of the dielectric number, respectively.

	Layer	Thickness [nm]	e'	e''
1	LaSFN9 glass	bulk	3.40	0
2	Cr	7.1	-6.30	30.75
3	Au	48.6	-12.30	1.26
4	Air	bulk	1.00	0
4	MeOH	bulk	1.75	0

Based on the parameters in Table 1, several SPR-spectra were simulated assuming a layer of organic material with the refractive index n = 1.45 (ε' = 2.10) and the layer thickness d = 0, 1, 2 and 4 nm being present between the gold layer and the solvent (Figure 4a). The simulated values for $R(q = 55.6°)$ were plotted against the layer thickness d assumed for the siumulation (Figure 4b). Calculation of the gradient of the plot in Figure 4b gave $\Delta R/\Delta d$ = (0.0247 ± 0.0014) mV nm^{-1}. This value in combination with the value $\Delta R_{\mathrm{PG_{5000}\text{-Thioc 5c}}} = (39 \pm 5)$ mV (extracted from Figure 2) allows to calculate the gain in layer thickness due to PG$_{5000}$-Thioc adsorption to d = (2 ± 1) nm. The uncertainty in layer thickness can be explained in terms of the uncertainty of the refractive index. Since the calculated value for d strongly depends on the assumed value for n, small variations in the latter value have significant impact on d.

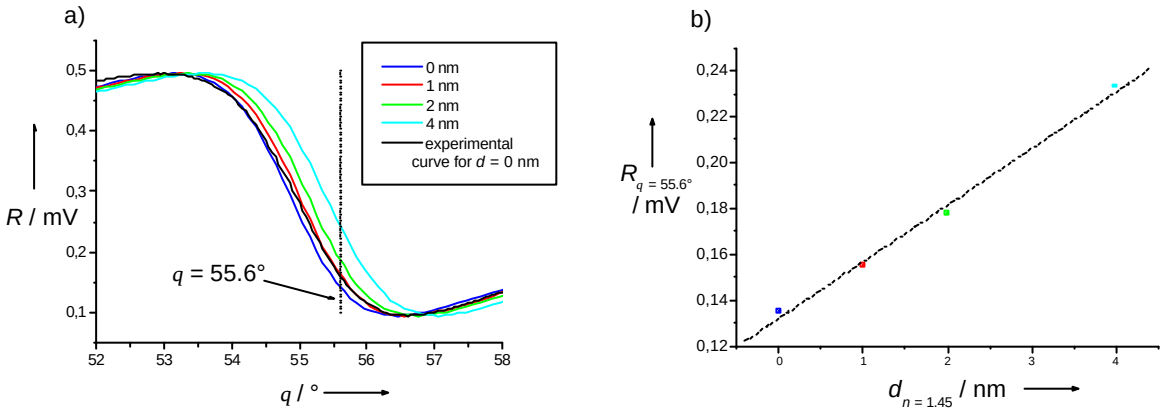

Figure 4. a) Simulated SPR-spectra for different layer thicknesses. b) Diagram showing the reflectivity of the SPR-substrate at the measuring angle q = 55.6° as a function of the simulated layer thickness. A linear fit of the 4 datapoints gave $\Delta R/\Delta d$ = (0.0247 ± 0.0014) mV nm^{-1}.