Polymer-supported alkyl monolayers on silica: synthesis and self-assembly of terminal functionalized poly(*N*-propionylethylenimine)s

Rainer Jordan,*[a] Karlheinz Graf,[b] Hans Riegler[c] and Klaus K. Unger[a]

[a] *Institut für Anorganische und Analytische Chemie, Universität Mainz, Becherweg 24, 55099 Mainz, Germany*
[b] *Institut für Physikalische Chemie, Universität Mainz, Welderweg 11, 55099 Mainz, Germany*
[c] *Max-Planck, Institut für Kolloid-und Grenzflächenforschung, Rudower Chaussee 5, 12489 Berlin/Adlershof, Germany*

A novel class of amphiphilic silane functionalized linear poly(*N*-propionylethylenimine)s (PPEIs) are synthesized by living polymerization of 2-ethyloxazoline and grafted onto silica substrates to form stable polymer supported alkyl monolayers (PSM) which may mimic biological membranes.

The formation of stable and organized layers of small amphiphilic molecules on solid substrates by Langmuir–Blodgett transfer and self-assembly has been investigated by numerous research groups.[1] One of the goals of this research is to obtain a system which mimics biological cell membranes. In this respect it is crucial to maintain a sufficient fluidity of the exposed alkyl layer without loosing the advantage of chemical fixation. To cope with substrate surface roughness or to incorporate biopolymers for sensor applications, polymer-supported monolayers were investigated.[2]

The living cationic ring-opening polymerization of 2-substituted 2-oxazolines provides synthetic possibilities to tailor a macromolecule, composed of a defined flexible linear hydrophilic polymer spacer (controlled chain length and narrow polydispersity) providing the mobility and appropriate functionalities for organization and chemical fixation at both terminal ends.[3,4]

Here we report a 'one-pot multi-step' reaction which results in a poly(*N*-propionylethylenimine) (PPEI) bearing a hydrophobic moiety on the distal side and a coupling group on the proximal side, Fig. 1(*a*). The alkyl moieties were introduced *via* fast initiation using hexadecyl- or 1,2-*O*-Dioctadecyl-*sn*-glycero-3-triflate[5] **1** as initiators. 4-Aminobutyldimethylmethoxysilane **4**, a monofunctional silane coupling group, was introduced *via* termination. The length of the polymer spacer could be adjusted by the initial monomer **2** to initiator ratios ($[M]_o/[I]_o$), Scheme 1. Almost quantitative conversions for **5** and the physicochemical characterization by ^1H and ^{13}C NMR, FTIR spectroscopy and mass spectrometry indicate the completeness of each reaction step.†

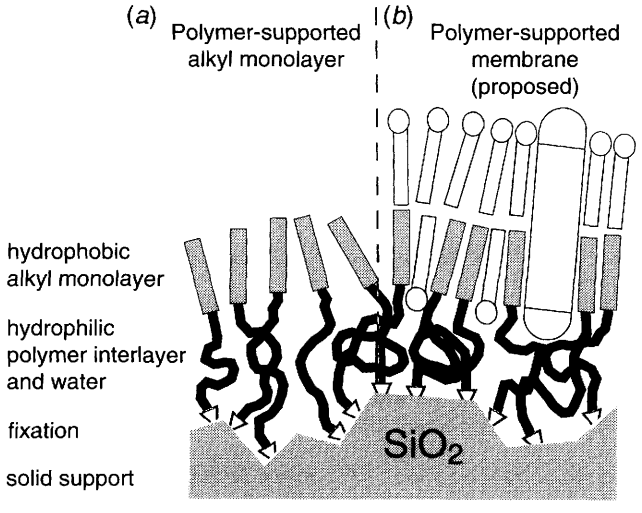
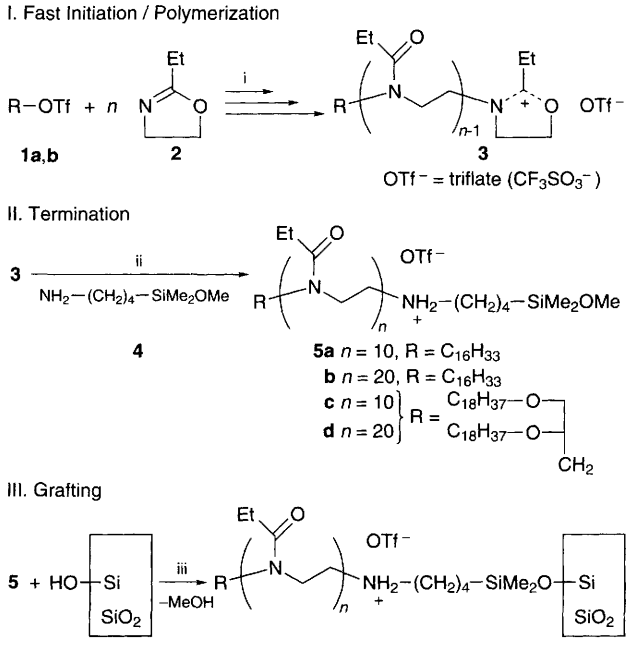


Fig. 1 (*a*) A schematic representation of the morphology of PSMs; (*b*) polymer-supported bilayers for the incorporation of membrane associated proteins based on PSMs

The grafting of **5** onto oxidized planar silicone wafers was carried out in a similar way to a previously reported procedure to ensure maximum ligand density.‡

The successful reaction was confirmed by the similarity of the bulk spectra[6] of the polymer with the attenuated total reflectance (ATR) FTIR spectra of the modified wafers. In all spectra the amide I band at 1640 cm^{-1} characterizes the presence of the tertiary amide group in the repeating unit of the polymer block.

A broad peak assembly dominates the CH-stretching region originating partly from the ethyl sidechain (2940 cm^{-1}, shoulder) and the methylene group of the polymer backbone (2880 cm^{-1}, shoulder).[7] Strong CH_2-stretching bands originating from the long alkyl moiety appear in the ATR spectrum of the PSM of **5a** at 2926 and 2855 cm^{-1} (bulk spectrum of **5a**: 2922 and 2853 cm^{-1}). These correspond to the asymmetric and symmetric CH_2-stretching modes characteristic for alkanes [$-(CH_2)_n-$ with $n > 4$] in a non-associated liquid-like state.[8] The band maxima of the CH_2-stretching modes of **5c** were at similar positions (2924 and 2853 cm^{-1}) also corresponding to a



Scheme 1 *Reagents and conditions*: i, 2-ethyloxazoline, alkyl triflate, $[M]_o/[I]_o$ ratio 10 : 1 for n = 10 and 20 : 1 for n = 20, MeCN, 0 °C–reflux, 48 h; ii, 0 °C, 4-aminobutyldimethylmethoxysilane **4**, 24 h at room temp., precipitation ($CHCl_3$–diethyl ether); iii, freshly activated silicone wafers and **5**, MeCN, reflux, 2 h

liquid-like state. In the bulk spectrum they are observed at 2918 and 2850 cm^{-1}, indicating saturated long chain alkanes in the crystalline state.§

X-Ray reflectivity measurements of the bulk samples of **5c** at room temperature show a series of Bragg peaks corresponding to *d*-spacings of 64 Å, which obviously originate from polymer amphiphile bilayers. The length of a fully stretched **5c** molecule was calculated to be 65–70 Å. Therefore, bilayers with interdigitated and/or tilted molecules or molecule sections can be assumed. Bulk samples of the other compounds showed no Bragg interferences which is in agreement with FTIR and DSC measurements, probably because of their non-crystalline ordering.

In X-ray reflectivity of PSMs pronounced Bragg minima were observed (Fig. 2) corresponding to spacings of 16.5 (**5a**), 11 (**5b**), 20 (**5c**) and 15 Å (**5d**) respectively. These spacings probably originate from the tilted alkyl moieties of the polymer amphiphiles. The tilting can be expected because of the larger cross section of PPEI chains compared to the alkyl chains. The tilt angle is also influenced by the packing restrictions (dynamics) of the alkyl chains. Interferences originating from the air–monolayer and monolayer–substrate interface can be expected at *q*-vectors below 0.1 $Å^{-1}$ (half a bilayer spacing is 32 Å as measured for the bulk sample **5c**). They are most likely not very pronounced because of the presumably small change in electron density and the rough substrate surface. In fact, there are clear indications of interference minima for the thinner PSMs (at q = 0.09 $Å^{-1}$ for **5d** and q = 0.1 $Å^{-1}$ for **5b** as pointed out in Fig. 2) which corroborate our interpretation.

Water wettability studies also confirmed the proposed morphology of the amphiphilic surface, Fig. 1(*a*). The advancing contact angles were between 60° and 80° while the receding contact angles were between 25° and 30°. This shows that the outer surface is hydrophobic and formed by the alkyl moieties. In agreement with the ATR spectra, the contact angles indicate that the alkyl monolayer is not organized in a dense and rigid alkyl chain packing. The pronounced hysteresis between the advancing and receding angles seems to be characteristic of PSM's.[2]

In summary, it is shown, that various functionalized linear polymer amphiphiles can be synthesized with well-defined ratios of hydrophilic and lipophilic moieties via living cationic polymerization of 2-ethyloxazolines. These polymer amphiphiles can be grafted onto silica surfaces to form organized polymer-supported alkyl monolayers. Due to the low toxicity of PPEI,[9] these PSMs may be suitable for the preparation of polymer supported membranes with incorporated proteins without loss of functionality, Fig. 1(*b*).

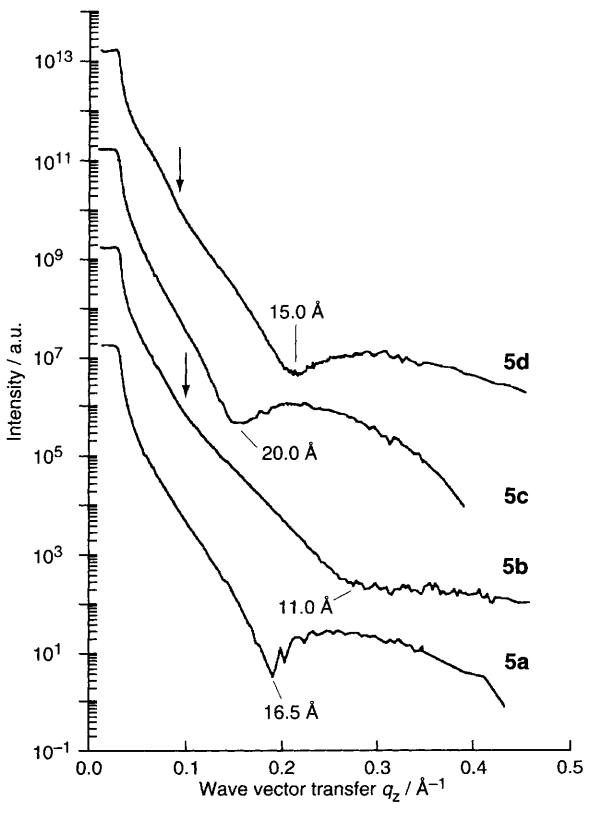


Fig. 2 Specular X-ray diffractograms of PSMs of **5a–d**. (Intensities were multiplied by factors of 100.)

Footnotes

† The degree of polymerization ($n \pm 3$) was calculated from ^{1}H NMR analysis {ratio of integrals from end-group signals around δ 0.0 [CH_2–$Si(CH_3)_2$, 6 H] *vs.* isolated signals from monomer units around δ 3.3 (CH_2–N–CH_2, 4 H, monomer unit} and are close to the $[M]_o/[I]_o$ ratio. Additionally, preliminary results from mass spectrometry confirmed a low polydispersity (1.03–1.13), the presence of both functionalizations and the polymerization degree calculated by NMR analysis.

‡ Optimization of conditions for the coupling reaction of silane functionalized PPEI on silica have been previously reported.[10] Maximum ligand densities (2–3 μmol m^{-2}) could be reached by using different catalysts solvents and activation of the silica surface by means of acid treatment. After modification, the wafers were extensively washed with polar organic solvents to remove physisorbed unreacted polymer. After analogue treatment of oxidized silicone wafers with PPEI polymer without a silane coupling group[11] the ATR spectrum did not display any significant adsorption bands.

§ Differential scanning calorimetry (DSC) and polarisation microscopy of the bulk samples verified this observation (T_g = 12 °C; T_m = 46 °C and a second phase transition at 52 °C; all other amphiphilic PPEIs had only glass transitions between 8° and 25 °C). Polarized microscopy studies showed bifringence as long as the alkyl chains were associated.

References

1 A. Ulman, *An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-assembly*, Academic Press Inc., Boston, 1991.

2 Chr. Erdelen, L. Häussling, R. Naumann, H. Ringdorf, H. Wolf, J. Yang, M. Liley, J. Spinke and W. Knoll, *Langmuir*, 1994, **10**, 1246 and references cited therein.

3 S. Kobajashi, S. Iijima, T. Igarashi and T. Saegusa, *Macromolecules*, 1987, **20**, 1729.

4 Y. Chujo, E. Ihara, H. Ihara and T. Saegusa, *Macromolecules*, 1989, **22**, 2040.

5 Initiators were prepared according to N. Ranganathan and B. T. Storey, *J. Heterocycl. Chem.*, 1980, **17**, 1069.

6 T. Saegusa, A. Yamada, H. Taoda and S.Kobayashi, *Macromolecules*, 1978, **11**, 435; B. L. Rivas and S. I. Ananias, *Polym. Bull.*, 1992, **28**, 3.

7 L. J. Bellamy, in *The Infra-red Spectra of Complex Molecules*, Chapman and Hall, London, 1975.

8 R. G. Snyder, H. L. Strauss and C. A. Elliger, *J. Phys. Chem.*, 1982, **86**, 5145.

9 M. C. Woodle, C. M. Engbers and S. Zalipsky, *Bioconjugate Chem.*, 1994, **5**, 493.

10 R. Jordan and K. K. Unger, *Oral Presentation and Poster No. 107; 12th ISPPP*, Dec. 1992, Sydney, Australia.

11 PPEI polymer analogue to **5** (R = Me; n = 10; initiator: methyltosylate) with a terminal hydroxy group was synthesized by aqueous work-up according to: S.Kobayashi, E. Masuda, D. Shoda and Y. Shimano, *Macromolecules*, 1989, **22**, 2878.

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