Lipopolymers for Surface Functionalizations. 1. Synthesis and Characterization of Terminal Functionalized Poly(*N*-propionylethylenimine)s

Rainer Jordan,*,† Kai Martin,# Hans Joachim Räder,# and Klaus K. Unger‡

Lehrstuhl für Makromolekulare Stoffe, Lichtenbergstr. 12, TU München, 85747 Garching, Germany, Department of Chemistry, Chemical Engineering and Material Science, Polytechnic University, Six Metrotech Center, Brooklyn, New York 11201, and NSF-MRSEC "Polymers at Engineered Interfaces"; Institut für Anorganische und Analytische Chemie, Duesbergweg 10-14, Johannes Gutenberg Universität Mainz, 55099 Mainz, Germany; and Max Planck-Institut für Polymerforschung, Ackermannweg 10, 55124 Mainz, Germany

Received September 5, 2001

ABSTRACT: By a direct combination of the fast initiation technique and a selective quantitative termination reaction, terminally functionalized poly(*N*-propionylethylenimine)s (PPEIs) were prepared by cationic living ring-opening polymerization of 2-ethyl-2-oxazoline in a one-pot multistep reaction. The chain ends of the linear hydrophilic polymers were functionalized with different lipophilic moieties (methyl-, *n*-hexadecyl- (C_{16}-), and 1,2-*O*-diooctadecyl-*sn*-glyceryl- ((C_{18})$_2$-)) and a monofunctional silane coupling group. Varying the length of the double functionalized hydrophilic PPEI chain (n = 10, 20), surface active amphiphilic lipopolymers of controlled hydrophilic lipophilic balance could be obtained in high overall yields. The spectroscopic, chromatographic, and mass spectrometric characterization confirmed that each reaction step was nearly quantitative and narrow molecular weight distributions (M_w/M_n = 1.07−1.24) of all polymers.

1. Introduction

The modification of solid substrates by end-grafted linear polymer chains is a very intriguing research field due to the unique properties of the resulting polymer brush-type modifications[1] and its potent applications in semiconductor processing, sensor development, the control of adhesion, and friction. Recently, we reported on the preparation of densely grafted polymer brush layers on planar substrates as well as nanoparticles using self-assembled monolayers as initiator systems for the so-called "grafting from approach".[2−4] Using this technique, polymer brushes of extremely high grafting densities can be prepared. However, because of the difficulty in determining the degree of polymerization, polydispersity, and composition of the surface bond polymers, a meaningful correlation between the polymer composition and the resulting structure and physical behavior of the polymer brush layer is rather difficult or based on estimations. The alternative route to obtain polymer brush systems is to synthesize an amphiphilic polymer equipped with a suitable coupling group, fully analyze the material, and chemisorb the macromolecules onto the surface ("grafting-onto" technique).

We followed this approach in a short summary of our findings on polymer-supported alkyl monolayers (PSMs) on planar silica substrates as well as in an in situ ellipsometry study of the swelling behavior of poly(2-alkyl-2-oxazoline) brush systems.[5−7]

We are especially interested in brush systems of hydrophilic poly(2-ethyl-2-oxazoline) derivatives because of its "biocompatibility"[8] and amorphous nature.[9,10] Similar to poly(ethylene oxide), surface modifications with homopolymer or amphiphilc poly(2-alkyl-2-oxazoline) lipopolymer brushes are under study to prepare functional surfaces for medical and biological applications or as compatibilizers for composite materials.[8−11]

In this paper we give a detailed account on the synthesis and physicochemical characterization of the silane functionalized lipopolymers as used for the preparation of the polymer-supported monolayers (PSMs). A schematic representation of such an end-functionalized lipopolymer is depicted in Figure 1.

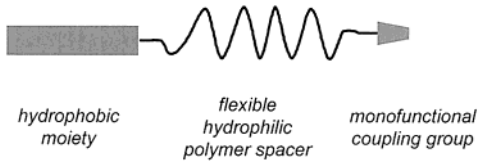

Figure 1. Cartoon of a functionalized lipopolymer for surface modification.

2. Experimental Section

2.1. Materials. All glassware used was allowed to bake at least overnight at 150 °C in order to remove traces of water and other impurities from the glass surface. All solvents except dry benzene, diethyl ether, and chloroform (SDS) were of LiChrosolv quality (E. Merck). Chloroform used for the polymerization was additionally purified, dried, and freshly distilled prior to use.

2-Ethyl-2-oxazoline (**4**) (Aldrich) was freshly distilled from KOH before polymerization.[12] 4-Aminobutyldimethylmethoxysilane (ABCR), 1-hexadecanol (Aldrich), and 1,2-*O*-dioctadecyl-*sn*-glycerol (BACHEM) were used without further purification. Methyl *p*-toluenesulfonate (**1a**) (Aldrich) was purified by distillation. All distillations and reactions were carried out under a dry nitrogen atmosphere.

† Lehrstuhl für Makromolekulare Stoffe, TU München; Polytechnic University, and NSF-MRSEC "Polymers at Engineered Interfaces".
‡ Institut für Anorganische und Analytische Chemie, Universität Mainz.
# Max Planck-Institut für Polymerforschung.
* To whom the correspondence should be addressed: phone: +49(0)89-289-13581; FAX -13562; E-mail Rainer.Jordan@ch.tum.de.

10.1021/ma011573e CCC: $20.00
Published on Web 11/21/2001

2.2. Methods and Instrumentation. *NMR Spectroscopy.* NMR spectra were recorded in $CDCl_3$ using a Bruker 200 MHz NMR spectrometer. ^{1}H NMR spectra used to calculate the degree of polymerization by end group analysis were recorded on a 400 MHz spectrometer (ASPECT 3000, Bruker).

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra were obtained by accumulating 500 scans at 4 cm^{-1} spectral resolution using a SpectraTech IR plane microscope setup connected to a Nicolet 5 SXB FTIR spectrometer equipped with a MCT-A detector cooled with liquid nitrogen.

The samples were prepared as a thin film from a concentrated chloroform or acetone solution onto a polished NaCl crystal, occupying roughly $^3/_4$ of the window. Backgrounds were recorded before every measurement on the same crystal using a clean spot.

MALDI TOF Mass Spectrometry. Mass measurements were performed using a Bruker REFLEX MALDI TOF mass spectrometer, equipped with a nitrogen laser (LSI, 337 nm, 3 ns pulse length) and two detectors. For external calibration polystyrene standard (Polymer Standard Service, Mainz, Germany) with $M_p = 2380$ g/mol was used. The mass accuracy determined was about 0.05%. The laser power was adjusted slightly above the threshold (10^6-10^7 W/cm^2). The ions were accelerated by a potential of 33.65 kV and reflected with a 35 kV potential.

For each spectrum 60 transients were accumulated. The resolution at $m/z = 2000$ was 500. To ensure that in the spectra recorded in reflection mode higher masses are not discriminated due to metastable decays, the samples were first measured in the linear mode using an HIMASS detector. Afterward, all spectra were recorded in the reflection mode, using a double-plate microchannel detector at the end of the second flight tube. However, spectra of all samples discussed in this paper did not show any significant difference if recorded in either of the two modes with respect of relative peak intensities and peak positions. Because of the better signal-to-noise ratio, only reflection spectra are presented here as used for the data evaluation.

Baseline correction and calculation of M_n, M_w, and M_p were carried out using the Bruker XMASS program.

1,8,9-Trihydroxyanthracene (Aldrich) was found to be a suitable matrix. It was dissolved in THF ($c = 25$ g/L) and mixed with the sample dissolved in THF ($c = 10^{-4}$ mol/L) in a 1:1 (v:v) ratio. Finally 1 μL of a $LiCF_3CO_2$ solution in THF ($c = 2$ g/L) was added and stirred shortly. The addition of a small amount of a lithium salt ensured a selective and quantitative ionization. A fraction of 1 μL of the final mixture was placed on a multistage target, air-dried, and transferred into the mass spectrometer.

Gel Permeation Chromatography. Gel permeation chromatography (GPC) was carried out on a Waters GPC 510 equipped with an UV and RI-detector and using polystyrene standards for calibration.

2.3. Synthesis. Preparation of Initiators.[13] *n-Hexadecyl Trifluoromethanesulfonate* (**3b**). To 4.7 g (0.034 mol) of anhydrous potassium carbonate and 2.1 g (0.009 mol) 1-hexadecanol (**1b**) in 10 mL of CH_2Cl_2, a mixture of 3 g (0.018 mol) of trifluoromethanesulfonic anhydride (**2**) in 5 mL of dry CH_2Cl_2 was added dropwise over 30 min at 0 °C. The reaction mixture was stirred overnight at 0 °C. The mixture was filtered under nitrogen (PTFE; 0.45 μm pore size, from Satorius) and washed several times with dry CH_2Cl_2. The solvent was removed slowly under reduced pressure at room temperature. The solid product was recrystallized twice from dry acetone and freeze-dried using dry benzene to give a colorless powder.

Yield: 98%. ^{1}H NMR (in $CDCl_3$): δ (ppm) 0.8 (t, C*H*$_3$−CH$_2$−; 3H), δ 1.2 (b, CH$_2$−(C*H*$_2$)$_{13}$−CH$_2$−, 26H), δ 1.7 (m, −C*H*$_2$−CH$_2$−O, 2H), 4.5 (t, C*H*$_2$−O).

^{13}C NMR ($CDCl_3$): δ (ppm) 13.63 (CH$_3$−), δ 22.4 (ω-CH$_2$−), δ 24.8 **(**$\omega + 1$ −CH$_2$−), δ 26.6/δ 27/δ 29.1/29.2 **(**−CH$_2$−**)**, δ 29.4 **(**β-CH$_2$−**)**, δ 31.7 (α-CH$_2$−).

1,2-O-Dioctadecyl-sn-glycero-3-trifluoromethanesulfonate (**3c**). **3c** was prepared in a similar manner using 1.23 g (0.002 mol) of 1,2-*O*-dioctadecyl-*sn*-glycerol (**1c**), 1 g (0.007 24 mol) of anhydrous potassium carbonate in 5 mL of dry CH_2Cl_2, and 0.8 g (0.003 mol) of trifluoromethanesulfonic anhydride (**2**) in 2 mL of dry CH_2Cl_2.

Yield: 97%. ^{1}H NMR (in $CDCl_3$): δ 0.9 (b, C*H*$_3$−(CH$_2$)$_{15}$−, 6H), δ 1.2 (b, CH$_2$−(C*H*$_2$)$_{15}$−CH$_2$−, 60H), δ 1.6 (b, −C*H*$_2$−CH$_2$−O−, 4H), δ 3.3−3.8 (m, −CH$_2$−C*H*$_2$−O−, −O−CH−C*H*$_2$−O−, −O−C*H*−CH$_2$−O−, 7H), δ 4.5 (d, C*H*$_2$−OTf, 2H). ^{13}C NMR (in $CDCl_3$): δ (ppm) 14.09 (CH$_3$−), δ 22.67 (ω-CH$_2$−), δ 25.9 **(**$\omega - 1$ −CH$_2$−), δ 29.35/δ 29.49/δ 29.68/δ 30.9 **(**−CH$_2$−**)**, δ 31.9 (α-CH$_2$−), δ 68.5/δ 71.0/δ 71.9 (−O−CH$_2$−/−O−CH=).

Standard Procedure of the Polymerization. In a dry nitrogen atmosphere 0.1 mol (for $n = 10$; 0.2 mol for $n = 20$) of 2-ethyl-2-oxazoline was added to a prepared solution of 0.01 mol of alkyl *p*-toluenesulfonate (**3a**) or alkyl trifluoromethanesulfonate (**3b,c**) in 20 mL of $CHCl_3$ at 0 °C using syringes. The reaction vessel was sealed and allowed to react under reflux. The time of polymerization depended on the initiator and desired polymerization degree (refer to Table 1 in the main section for further details).

Termination. *Silane Functionalized R-PPEI$_n$-Si.* The reaction mixture was cooled to 0 °C, and 0.02 mol of 4-aminobutyldimethylmethoxysilane (**7**) was added. The temperature was elevated instantly to room temperature. After 72 h, the solution was transferred into 200 mL of dry and degassed diethyl ether to precipitate a white powder. After two reprecipitation procedures ($CHCl_3$/diethyl ether) the final product was collected and freeze-dried (dry benzene) to give in all cases a hygroscopic colorless powder.

PPEI$_{10}$-Si (**8c**). Yield (calcd against initiator, obtained yield collected after reprecipitation): 98%. ^{1}H NMR (in $CDCl_3$) δ (ppm): δ −0.2−0.0 (m, CH$_2$−Si(C*H*$_3$)$_2$, 6H), δ 0.5 (b, C*H*$_2$−Si-(CH$_3$)$_2$, 2H), δ 0.9−1.1 (b, C*H*$_3$−CH$_2$−CO−N), δ 2.0−2.4 (b, CH$_3$−C*H*$_2$−CO−N), δ 2.2 (s, *p*-C*H*$_3$−C$_6$H$_4$SO$_3$−), δ 2.9 (m, C*H*$_3$−N−CO−), δ 3.1−3.5 (b, C*H*$_2$−N−C*H*$_2$), δ 7.1 and 7.6 (AA′ XX′ system, aromatic, *p*-C*H*$_3$−C$_6$*H*$_4$−SO$_3$−). ^{13}C NMR (in $CDCl_3$): δ (ppm) 0.24 (CH$_2$−Si(*C*H$_3$)$_2$), δ 15.47 (*C*H$_2$−Si(CH$_3$)$_2$), δ 19.81 (*C*H$_2$−CH$_2$−Si(CH$_3$)$_2$), δ 36.9 (N−CH$_2$−*C*H$_2$−), δ 39.87 (N−*C*H$_2$−CH$_2$−), δ 43.63 (*C*H$_3$−CH$_2$−CO−N), δ 45.42 (CH$_3$−*C*H$_2$−CO−N), δ 47.14 (*C*H$_2$−N−CH$_2$), δ 59.14 (*C*H$_3$−N), δ 173.9 + 174.12 + δ 174.52 (=N−*C*=O−CH$_2$−). Anal. Calcd for $C_{65}H_{128}N_{11}O_{14}SSi$ (FW: 1347.94) (in %): C, 57.92; H, 9.57; N, 11.43. Found: C, 56.95; H, 9.50; N, 11.28.

C$_{16}$-PPEI$_{10}$-Si (8a): Yield (calcd against initiator): 88%. ^{1}H NMR (in $CDCl_3$) δ (ppm): δ −0.2−0.1 (m, CH$_2$−Si (C*H*$_3$)$_2$, 6H), δ 0.5 (b, C*H*$_2$−Si(CH$_3$)$_2$, 2H), δ 0.9 (t, *CH*$_3$−CH$_2$−), 1.0−1.2 (b, C*H*$_3$−CH$_2$−CO−N), δ 1.1−1.3 (b, −(CH$_2$)$_n$), δ 2.1−2.4 (b, CH$_3$−*CH*$_2$−CO−N), δ 3.1−3.6 (b, *CH*$_2$−N−*CH*$_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) −0.25 (CH$_2$−Si(*C*H$_3$)$_2$), δ 14.63 (CH$_3$−), δ 17.82 (*C*H$_2$−Si(CH$_3$)$_2$), δ 20.38 (*C*H$_2$−CH$_2$−Si(CH$_3$)$_2$), δ 22.3 (ω-*C*H$_2$−), δ 24.6 **(**$\omega + 1$ −CH$_2$−), weak signals ~ δ 29 (β-*C*H$_2$−, α-*C*H$_2$−**,** ω-*C*H$_2$), δ 29.2 (−*C*H$_2$−), δ 43.46 **(***C*H$_3$−CH$_2$−CO−N**)**, δ 45.25 (CH$_3$−*C*H$_2$−CO−N), δ 47.1 **(***C*H$_2$−N−*C*H$_2$), ~ δ 174.5 two peaks (=N−*C*=O−CH$_2$−). Anal. Calcd for $C_{74}H_{142}F_3N_{11}O_{14}SSi$ (FW: 1527.15) (in %): C, 58.19; H, 9.38; N, 10.03. Found: C, 55.34; H, 9.67; N, 10.23.

C$_{16}$-PPEI$_{20}$-Si (**10**): Yield (calcd against initiator): 74%. ^{1}H NMR (in $CDCl_3$) δ (ppm): δ −0.1−0.1 (m, CH$_2$−Si(C*H*$_3$)$_2$, 6H), δ 0.5 (m, *CH*$_2$−Si (CH$_3$)$_2$, 2H), δ 0.85 (t, *CH*$_3$−CH$_2$−), 1.0−1.2 (b, C*H*$_3$−CH$_2$−CO−N), δ 1.1−1.3 (b, −(CH$_2$)$_n$), δ 2.1−2.5 (b, CH$_3$−*CH*$_2$−CO−N), δ 3.2−3.6 (b, *CH*$_2$−N−*CH*$_2$). Anal. Calcd for $C_{124}H_{232}F_3N_{21}O_{24}SSi$ (FW: 2518.47) (in %): C, 59.12; H, 9.29; N, 11.68. Found: C, 58.17; H, 10.06; N, 11.98.

(C$_{18}$)$_2$-PPEI$_{10}$-Si (**8b**): Yield (calcd against initiator): 97%. ^{1}H NMR (in $CDCl_3$) δ (ppm): δ −0.1−0.1 (m, CH$_2$−Si(C*H*$_3$)$_2$, 6H), δ 0.4−0.5 (m, *CH*$_2$−Si(CH$_3$)$_2$, 2H), δ 0.85 (t, *CH*$_3$−CH$_2$−), 1.0−1.2 (b, C*H*$_3$−CH$_2$−CO−N), δ 1.1−1.3 (b, −(CH$_2$)$_n$), δ 2.0−2.5 (b, CH$_3$−*CH*$_2$−CO−N), δ 3.0−3.5 (b, *CH*$_2$−N−*CH*$_2$). ^{13}C NMR (in $CDCl_3$): δ (ppm) −0.25/−0.28 (CH$_2$−Si(*C*H$_3$)$_2$), δ 14,10 (CH$_3$−), δ 17.89 (*C*H$_2$−Si(CH$_3$)$_2$), δ 20.38 (*C*H$_2$−CH$_2$−Si(CH$_3$)$_2$), 22.67 (ω-CH$_2$−), 25.94 ($\omega - 1$ −CH$_2$−), 29.34/29.49/29.69/30.19 (−CH$_2$−), 31.9 (α-CH$_2$−**)**, δ 43.46 **(**CH$_3$−CH$_2$−CO−N**)**, δ 45.25 (CH$_3$−*C*H$_2$−CO−N), δ 47.1 (*C*H$_2$−N−*C*H$_2$), ~ δ 70.9 several peaks (O−CH$_2$−/O−CH = /N−CH$_2$), δ 173.9 + δ 174.12 + δ 174.50 (=N−*C* = O−CH$_2$−). Anal. Calcd for

Table 1. Parameters for the Synthesis of the Silane Functionalized Lipopolymers and Comparison of the Degrees of Polymerization as Determined by NMR, MALDI, TOF Mass Spectrometry, and Gel Permeation Chromatography

polymer	reaction time [days] polym	reaction time [days] term	initiator	$[M]_0/[I]_0$	^{1}H NMR[a]	MALDI[b]	GPC	termination with	yield[c] [%]
$PPEI_{10}$-OH (**9**)	2	2	**3c**	10	10	13	16	H_2O	97
$PPEI_{10}$-Si (**8c**)	2	2	**3c**	10	9	11	11	**7**	98
C_{16}-$PPEI_{10}$-Si (**8a**)	2.5	2	**3a**	10	10	10	14	**7**	88
C_{16}-$PPEI_{20}$-Si (**10**)	3	4	**3a**	20	17	21	28	**7**	74
$(C_{18})_2$-$PPEI_{10}$-Si (**8b**)	3	2	**3b**	10	6.5	10	12	**7**	97
$(C_{18})_2$-$PPEI_{20}$-Si (**11**)	3	4	**3b**	20	17	19	39	**7**	70

[a] For determination of DP ($n \pm 1$) was calculated from ^{1}H NMR analysis: Ratio of end group signals around δ 0.0 (CH_2−Si(CH_3)$_2$−, 6H) vs isolated signals from monomer units around δ 3.3 (CH_2−N−CH_2, 4H/monomer unit). [b] Calculated from the mass value of the most intense signal. [c] Yield after reprecipitation calculated vs initial amount of initiator.

$C_{97}H_{191}F_3N_{11}O_{16}SSi$ (FW: 1884.79) (in %): C, 61.81; H, 10.21; N, 8.17. Found: C, 60.44; H, 10.55; N, 8.12.

$(C_{18})_2$-PPEI$_{20}$-Si (**11**): Yield (calcd against initiator): 70%. ^{1}H NMR (in $CDCl_3$) δ (ppm): δ 0.0−0.2 (m, CH_2−Si(CH_3)$_2$, 6H), δ 0.5−0.6 (m, CH_2−Si(CH_3)$_2$, 2H), δ 0.9−1.3 (b, CH_3−CH_2−CO−N, CH_3−CH_2−, −$(CH_2)_n$), δ 2.1−2.5 (b, CH_3−CH_2−CO−N), δ 3.2−3.6 (b, CH_2−N−CH_2). Anal. Calcd for $C_{147}H_{281}F_3N_{21}O_{26}SSi$ (FW: 2876.11) (in %): C, 61.39; H, 9.85; N, 10.23. Found: C, 58.99; H, 10.09; N, 12.47.

PPEI$_{10}$-OH (**9**): PPEI polymer analogue to **8c** (R = CH_3−; n = 10; initiator: methyltosylate) with a terminal hydroxyl group was synthesized by aqueous workup using MeOH and KOH.[14] Yield (calcd against initiator): 97%. ^{1}H NMR (in $CDCl_3$) δ (ppm): δ 0.8−1.1 (b, CH_3−CH_2−CO−N), δ 2.0−2.4 b, CH_3−CH_2−CO−N), δ 2.9 (m, CH_3−N−CO−), δ 3.1−3.5 (b, CH_2−N−CH_2). ^{13}C NMR (in $CDCl_3$): δ (ppm) 43.7 (CH_3−CH_2−CO−N), δ 45.35 (CH_3−CH_2−CO−N), δ 47.1 (CH_2−N−CH_2), δ 59.14 (CH_3−N), δ 174.0 + δ 174.48 (=N−C=O−CH_2−). Anal. Calcd for $C_{51}H_{94}N_{10}O_{11}$ (FW: 1023.37) (in %): C, 59.86; H, 9.26; N, 13.69. Found: C, 57.04; H, 9.29; N, 11.36.

3. Results and Discussion

Saegusa et al. reported a convenient method for the introduction of terminal alkyl moieties via the fast initiator method.[15] There, the cationic ring-opening polymerization of 2-alkyl-2-oxazolines is initiated by alkyl trifluoromethanesulfonate (alkyl triflate). Compared to the normally used *p*-toluenesulfonate, the initiation step is much faster, and therefore a better control of the degree of polymerization and lower polydispersities was observed. During own preliminary synthetic efforts we indeed observed that, instead of tosylate, alkyl triflate initiators ensure a fast and quantitative initiation reaction for initiator systems bearing longer alkyl chains. This was confirmed by Kuhn et al. while using an analogue initiation system for the preparation of lipopolymers.[16]

The introduction of a silane coupling group can be achieved by a quantitative termination reaction of the living polymerization using primary amine compounds as an effective nucleophile.[17] Here, the first in dept study of the termination reaction of model compounds of 2-alkyl-2-oxazolines by Nuyken et al.[18] has to be mentioned. Side reactions were observed during the termination step using various nucleophiles due to the ambident character of 2-substituted 2-oxazolines. Litt et al. reported on the somehow limited polymerization degree of poly(2-alkyl-2-oxazoline)s due to chain transfer reactions.[19,20]

The reaction pathway employed to synthesize the silane functionalized polymer amphiphiles is presented in Figure 2. The combination of the functionalization techniques via the fast initiation and the termination reaction required modified reaction conditions. Using acetonitrile as the common solvent for the polymerization of 2-oxazolines resulted in low yields and presumably broad polydispersities. This can be attributed to the low solubility of the hydrophobic alkyl triflate initiator in acetonitrile at the reaction temperatures. The reaction mixtures became inhomogeneous due to the precipitation of the hydrophobic initiator, and therefore the initiation did not start uniformly. Chloroform was found to keep the growing polymer in solution even during the cooling step between the propagation and termination step. Performing the synthesis at reflux temperature of chloroform was found to be sufficient to start and propagate the living cationic polymerization at convenient ratios.

As shown in Table 1, in most cases the conversions for each reaction step were nearly quantitative, resulting in high overall yields for the final products. The end group analysis by ^{1}H NMR spectroscopy using the ratio of end group signals around δ 0.0 (CH_2−Si(CH_3)$_2$−; 6H) vs isolated signals from the monomer unit at δ 3.3 (CH_2−N−CH_2, 4H/monomer unit) calculates in some cases to slightly lower degrees of polymerization (DP) as expected from the initial monomer/initiator ratio ($[M_0]/[I_0]$) for products with a DP around 10. All three methods used for analysis of the polymer gave reasonable results, confirming a good control of the living polymerization. The deviations noticeable for the GPC results are discussed at the end of this section. Targeting higher DP, the deviation between calculated and determined values increased as reported previously by Litt et al.[21]

However, as listed in the Experimental Section, all signals of the ^{13}C and ^{1}H NMR spectra could be assigned and indicate a successful introduction of both functionalizations and a propagation reaction without side reactions based on the NMR analysis. To complete the physicochemical characterization, FTIR spectroscopy studies were carried out.

Consulting the literature, little can be found regarding the FTIR spectroscopy analysis of 2-oxazoline-based polymers. Considering the synthetic possibilities of the cationic ring-opening polymerization of this class of polymers, a detailed account of spectra analysis would help to identify and characterize such compounds. Here we will give a more detailed discussion of FTIR spectra and tentative assignments of characteristic bands especially in the fingerprint region. In this discussion, initial compounds such as 1-hexadecanol (C_{16}−OH) and 1,2-*O*-dioctadecyl-*sn*-glycerol ((C_{18})$_2$−OH), the aminosilane compound and poly(*N*-propionylethylenimine) with a terminal hydroxyl group ($PPEI_{10}$−OH) are included for comparison.

Figure 3 shows the row of transmission FT-IR spectra of the hydroxyl-terminated homopolymer $PPEI_{10}$−OH,

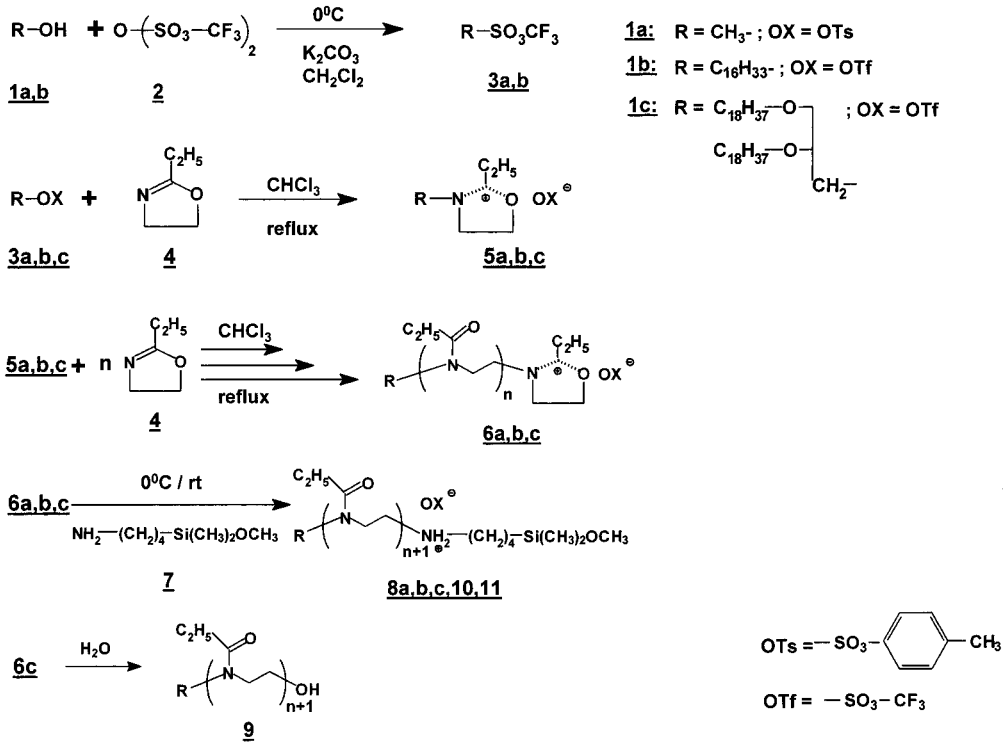

Figure 2. Reaction scheme for the preparation of poly(*N*-propionylethylenimine)s with various functionalities at the terminal ends. The hydrophobic moiety was introduced by means of the fast initiation reaction; the monofunctional silane coupling group for a controlled attachment onto a silica substrate was attached via a quantitative termination reaction using a nucleophilic primary amine group.

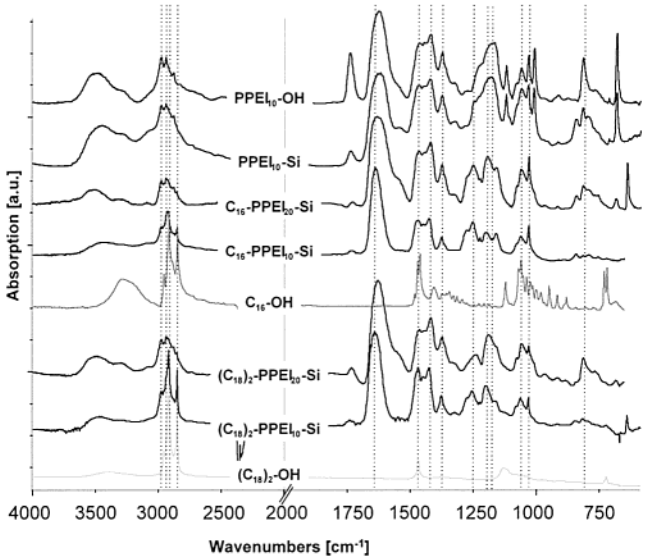

Figure 3. Transmission FTIR spectra of all polymers in the spectral range from 4000 to 600 cm^{-1}. For better comparison the spectra of the alcohols used for the initiators are depicted (gray lines). For exact positions of band maxima refer to Table 2.

PPEI bearing a silane coupling group ($PPEI_{10}$−Si), as well as the spectra of the lipopolymer with additional hydrophobic moieties and variation of the length of the polymer part. The positions of the band maxima and their assignments are listed in Table 2.[22−24] Starting with the spectrum of the PPEI homopolymer, the spectrum is very similar to the FTIR spectrum of PPEI or its homologue poly(*N*-acetylethylenimine) previously discussed in the literature.[25,26]

In the spectra of $PPEI_{10}$-OH and the silane functionalized $PPEI_{10}$-Si a broad peak assembly dominates the CH stretching region (3000−2800 cm^{-1}). The three peak maxima originating from the ethyl group of the acyl side chain and ethylene groups of the polymer backbone.[22] With increasing ratio of CH_x groups of the terminal *n*-alkyl moiety, additional sharper peaks at 2927 and 2856 cm^{-1} appear, corresponding to the asymmetric and symmetric CH_2 stretching modes characteristic for saturated long chain *n*-alkanes ($(CH_2)_n$; $n > 4$) in a liquidlike state.[27] The appearing asymmetric and symmetric CH_3 stretching bands at 2956 and 2874 cm^{-1} could be unambiguously assigned to the methylene groups situated in the terminal *n*-alkyl moieties by the direct comparison with the spectra of the related alcohols. An interesting feature displays the spectrum of $(C_{18})_2$-$PPEI_{10}$-Si. As in the spectrum of the pure alcohols the asymmetric and symmetric CH_2 stretching bands has their band maxima at 2918 and 2850 cm^{-1}, indicating that either only the alkyl chains or the complete polymer are in a crystalline state. This subject will be addressed in an upcoming paper.[28]

For all PPEI-containing compounds, the very strong amide I band (C=O stretching) around 1640 cm^{-1} characterize the presence of the tertiary amide group in the repeating unit of the polymer. The relative intensity of this band vs the alkyl stretching bands reflects the different polymerization degrees.

In the CH deformation region, all polymer-containing compounds displaying four assignable adsorption bands. The CH_2 scissor band at 1470 cm^{-1} is becoming stronger and sharper with increasing *n*-alkyl content and the spectrum of $(C_{18})_2$-OH has at 1467 cm^{-1} its peak maximum. The shoulder at 1458 cm^{-1} originates from the asymmetric CH_3 deformation mode, which is very strong for all other spectra. A third strong band at 1426−1420 cm^{-1} can be attributed to the CH_2 deformation of methyl groups of the acyl side chain. The

Table 2. Tentative Assignments for the IR Band Maxima for All Products

	position of band maxima [cm^{-1}][b]							
assignment[a]	$PPEI_{10}$-OH	$PPEI_{10}$-Si	$C_{16}PPEI_{20}$-Si	$C_{16}PPEI_{10}$-Si	$(C_{18})_2PPEI_{20}$-Si	$(C_{18})_2PPEI_{10}$-Si	$(C_{18})_2OH$	$C_{16}OH$
$\nu_{s,as}$(CH) of	2977 s	2977 s	2977 s	2977 s	2977 s	2977 m		
CH_3-CH_2-CO	2940 s	2941 s	2940 s	2940 s	2940 sh	2940 sh		
and -CH_2-N	2880 m	2880 m	2880 m	2880 m	2880 w	2880 sh		
$\nu_{as}(CH_3)$	n.a.	n.a.	2956 sh	2956 sh	2956 sh	2956 sh	2956 w	2955 s
$\nu_{as}(CH_2)^l$			2927 sh	2927 m	292 sch			
$\nu_{as}(CH_2)^s$						2918 s	2917 s	2917 s
$\nu_s(CH_3)$					2874 sh	2874 sh	2874 w	2874 w
$\nu_s(CH_2)^l$			2856sh	2856 s	2856 s			
$\nu_s(CH_2)^s$						2850 s	2851 s	2849 s
ν(CO)amide I	1642 s,br	1642 s,br	1642 s,br	1642 s,br	1642 s, br	1642 s, br		
$\delta(CH_2)$	1470 sh	1470 s	1470 s	1473−1468 s	1473−1467 s	1469 s	1467 s	1472 s
1462 s								
$\delta_{as}(CH_3)$	1448s	1451 s	1451s	1451 s	1451s	1451 s	1452 sh	1451 sh
δ(CH_2-CO)	1421s	1426 s	1421s	1426 s	1426s	1426 s		
$\delta_s(CH_3)$	1375s	1377 s	1375 s	1376 s	1378 s	1377 s	1378 w	
$\delta_s(CH_3)$ of			1255 sh	1255 sh	1255 sh	1255 sh		
$Si(CH_3)$		1255 sh						
$\delta(CH_2)$ of (CH_2)-Si		1061 sh,b	1061 sh,b	1061 sh,b	1061 sh,b	1061 sh,b		
1031 sh,b	1031 sh,b	1031 sh,b	1031 sh,b	1031 sh,b				
r (CH_2)			720 m	720 m	720 m	720 m	722 m	730 s +
								722 s
‘PPEI/OTf$^-$			1277 s	1277 s	1277 s	1277 s		
1200 s,br	1200 s,br	1200 s,br	1200 s,br	1200 s,br	1200 s,br			
1122	1122	1130 m	1124 m					
1080 sh	1080 sh	1080 sh	1080 sh	1080 sh	1080 sh	1080 w		
1065 m	1065 m	1065 m	1065 m	1065 m	1065 m			
1030 s	1030 s	1030 s	1030 s	1030 s	1030 s			
PPEI/OTs$^-$	1010	1010						

[a] ν_{as} = asymmetric valence mode; ν_s = symmetric valence mode; δ_{as} = asymmetric deformation mode; δ_s = symmetric deformation mode; r = rocking mode. [b] s = strong; m = medium; w = weak; sh = shoulder; br = broad; n.a. = not assignable due to overlap with neighboring bands.

symmetric CH_3 deformation appears at all spectra closely around 1375 cm^{-1}. From direct comparison with a spectrum of the pure silane coupling group (**4**), the characteristic symmetric CH_3 deformation band at 1256 cm^{-1} of the $-Si(CH_3)_2-$ group as well as weak or obscured bands of the methylene group attached to the silicon (1061 and 1031 cm^{-1}) could be identified in the corresponding spectra, proving a successful functionalization via the termination reaction (see Figure 3 and Table 2).

Despite several possible combinations of assignments for the five to eight following strong bands, a definite correlation to vibration modes cannot be made due to the complexity of the investigated molecules. At 720 cm^{-1} all PPEI spectra display a narrow single band corresponding to the CH_2 rocking mode.

On the basis of the results of NMR and FTIR spectroscopy that a terminal functionalization occurred, the analysis of the MALDI TOF mass spectra were used for critical discussion of the completeness of the reaction. The mass spectra for selected polymers are presented in Figures 4−6 along with an expanded view for detailed analysis.

In every spectrum one main population (α) is dominating. The spacings of Δ *m*/*z* signals in the rage between 99.15 and 99.38 are in good agreement with the expected mass of one monomer unit calculating to 99.13. This confirms that all products consist of one homologue series of the functionalized polymers. On the basis of the spectroscopy results, it can be assumed that all polymeric products are bearing the desired end functionalities. Calculating the total integral ratio of the peaks in the mass spectra between the main and side populations (β,β',γ), an overall portion of side product of 3−4.5% was found. In other words, more than 95% of the isolated product is homogeneously functionalized. The only exception was C_{16}-$PPEI_{10}$-Si where a multimodal distribution was observed (Figure 5).

In the MALDI TOF mass spectra of $PPEI_{10}$-OH and $PPEI_{10}$-Si, three populations could be identified. The mass difference of Δ m/z = 14 (α−β) can be explained by the initiation of the polymerization by a proton or hydrolysis of the methoxysilane to the silanol group. The γ population with $\Delta m/z$ = 56 is also present in all spectra. The intensities follows not in every case the intensities of the α population. Despite several attempts, a definite assignment was not possible.[29]

As mentioned above, the mass spectrum of C_{16}-$PPEI_{10}$-Si displays a multimodal distribution. The spectrum consists of a main population (1) of polymer homologues of the desired functionalities and polymerization degree. The species of population 2 lacking the terminal *n*-hexadecyl chain and bearing a proton instead, 3 is most likely a homologue series of dimers of population 2 where two living ends reacted with a single primary amino group of the terminating agent. Population 4 originates from the analogue dimer of hexadecyl-functionalized polymers. However, as displayed in Figure 5, the dominating species is the desired product, and therefore this material was used for further studies.Attributable species for the spectra of C_{18}-$PPEI_{10}$-Si and C_{18}-$PPEI_{20}$-Si are of the same origin as for the previously discussed mass spectra. Examination of the mass spectra revealed no further signals in higher mass regions. Thus, a coupling by a hydrolysis/condensation reaction of two terminal silane groups was not observed.

The determined M_p values (mass at peak maximum of the most intensive signal), the number-average molecular weight (M_n), and weight-average molecular weight (M_w) and the polydispersity index (PDI) are given in Table 3.[30] All products display a narrow polydispersity that slightly increases for polymers with

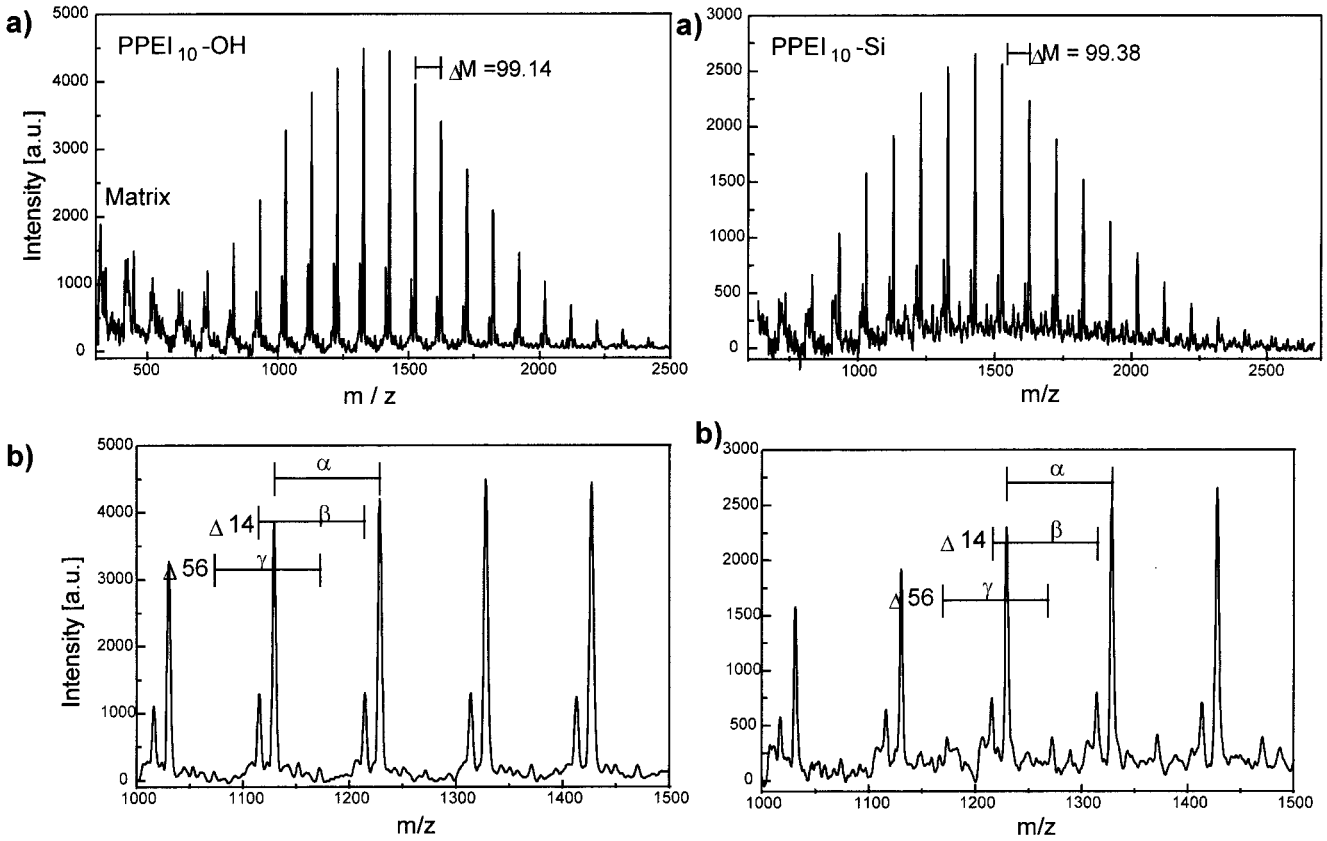

Figure 4. MALDI TOF MS spectrum of the monofunctionalized PPEIs (a) along with a detailed view (b).

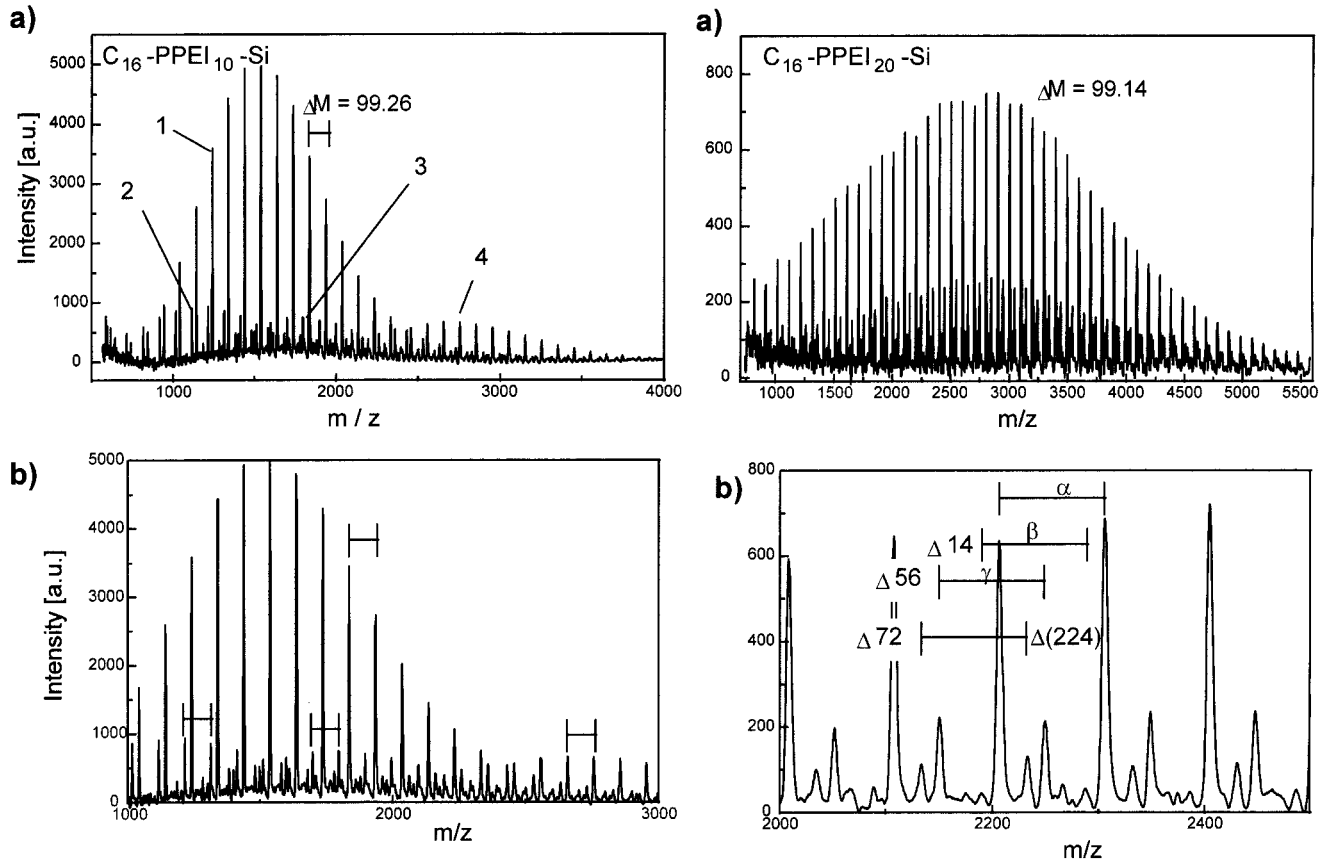

Figure 5. MALDI TOF MS spectrum of C_{16}-PPEI$_n$-Si with $n = 10$ (a, left) and $n = 20$ (a, right) along with a detailed view (b).

a DP around 20. The polymerization degree of the final lipopolymers could be well controlled by means of the initial monomer/initiator ratio. Polymorphic species could not be observed besides traces.

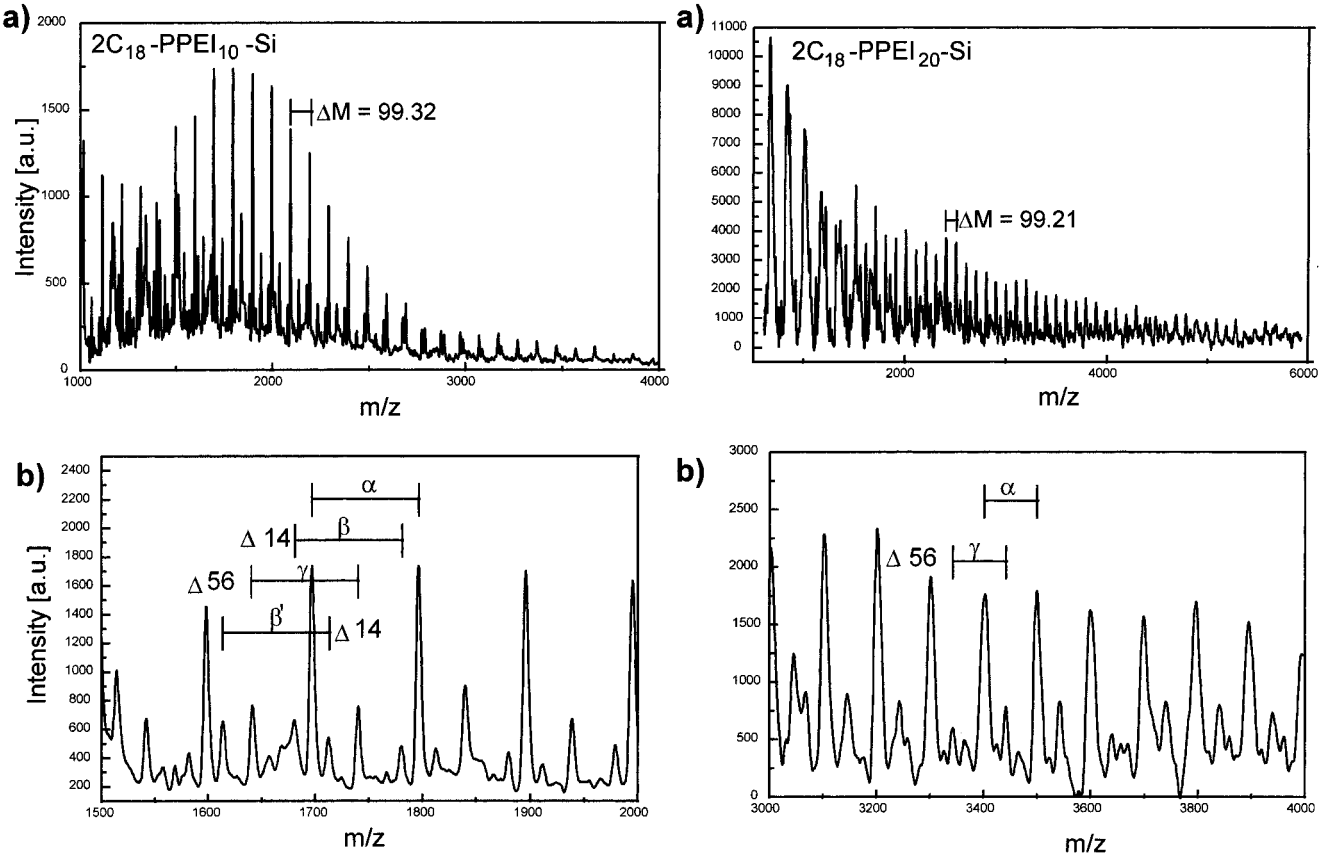

Figure 6. MALDI TOF MS spectrum of $(C_{18})_2$-PPEI$_n$-Si with $n = 10$ (a, left) and $n = 20$ (a, right) along with a detailed view (b).

Table 3. Analytical Data As Derived from the Respective MALDI TOF MS along with the Results from the GPC Measurements for Comparison (PDI = M_w/M_n; Polydispersity Index)

					MALDI TOF MS					GPC		
polymer	ΔM_{theor}[a] [g/mol]	ΔM_{exp}[b] [g/mol]	RM_{theor}[c] [g/mol]	RM_{exp}[b] [g/mol]	M_{theor}[j] [g/mol]	M_n [g/mol]	M_w [g/mol]	M_p [g/mol]	PDI	M_n [g/mol]	M_w [g/mol]	PDI
$PPEI_{10}$-OH	99.13	99.15	39.24[d]	38.81	1327.65	1274	1454	1326	1.14	1674	1825	1.09
$PPEI_{10}$-Si	99.13	99.38	340.46[e]	336.43	1427.59	1434	1554	1427	1.08	1424	1530	1.07
C_{16}-$PPEI_{10}$-Si	99.13	99.26	549.12[f]	546.42	1538.91	1780	2167	1483	1.22	2123	2480	1.17
C_{16}-$PPEI_{20}$-Si	99.13	99.14	521.48[g]	521.03	2603.34	2536	3144	2700	1.24	3454	4581	1.33
$(C_{18})_2$-$PPEI_{10}$-Si	99.13	99.33	903.38[h]	902.56	1895.95	2085	2289	1792	1.10	2343	2727	1.16
$(C_{18})_2$-$PPEI_{20}$-Si	99.13	99.21	918.15[i]	920.09	2806.97	2862	3411	2500	1.19	5759	7556	1.31

[a] ΔM = mass of the monomer unit. [b,c] ΔM_{exp} = slope and RM = residual mass; RM_{exp} = axis hit according to $y = \Delta M_{theor} n + RM_{theor}$ for the following species: [d] $[CH_3\text{-}(M)_n\text{-}OH\ ]\ Li^+$. [e] $[CH_3\text{-}(M)_n\text{-}NH_2^+\text{-}(CH_2)_4\text{-}Si(CH_3)_2\text{-}OH/OTs^-]\ Li^+$. [f] $[C_{16}H_{33}\text{-}(M)_n\text{-}NH\text{-}(CH_2)_4\text{-}Si(CH_3)_2\text{-}OCH_3/OTf^-Li^+]\ Li^+$. [g] $[C_{16}H_{33}\text{-}(M)_n\text{-}NH_2^+\text{-}(CH_2)_4\text{-}Si(CH_3)_2\text{-}OH/OTf^-]\ Li^+$. [h] $[C_{39}H_{82}O_2\text{-}(M)_n\text{-}NH{-}(CH_2)_4\text{-}Si(CH_3)_2\text{-}OCH_3/OTf^-Li^+]\ Li^+$. [i] $[C_{39}H_{82}O_2\text{-}(M)_n\text{-}NH\text{-}(CH_2)_4{-}Si(CH_3)_2\text{-}OCH_3/OTf^-Li^+]\ Na^+$. [j] Calculated mass with a degree of polymerization nearest to the measured value.

It is noteworthy that the polymerization degree determined by ^{1}H NMR end group analysis calculates to lower degrees than the values obtained by MALDI TOF mass spectrometry. In our opinion the mass spectroscopic values are more reliable because the end group signals of the dimethylsilane group or the methoxysilane group are relatively weak in comparison to the used signals from the monomer unit. Using the compositions determined by MALDI TOF MS for comparison with results of the elemental analysis (listed in the Experimental Section) gave also a better agreement than NMR based calculations. M_n and M_w values as obtained by GPC are in most cases comparable to the results derived from NMR or MALDI TOF MS. Here it is noteworthy that in the case of hydrophilic poly(2-oxazoline)s the absolute number- and weight-average values may vary strongly due to the calibration of the GPC system using polystyrene.[31] However, the polydispersity indices (Table 1) as calculated from the GPC traces were found to be more reliable than PDI values calculated from MALDI TOF MS spectra due to possible discrimination of low molar mass species and mass cutoff to eliminate mass signals of the matrix.

4. Conclusions

In summary, a straightforward one-pot synthesis is presented to obtain linear lipopolymers substituted with functional groups at both extremities. The introduction of a silane coupling group gives the possibility to form amphiphilic polymer brush type layers by terminal grafting onto a solid support. The introduction and variation of the hydrophobic moiety via the initiator method and a precise control of the hydrophilic polymer chain length results in amphiphilic lipopolymers which enables a systematic study of the influence of the hydrophilic lipophilic balance (HLB) upon the layer morphology of amphiphilic polymer brush systems.

This aspect will be addressed in upcoming papers using the presented compounds.

Acknowledgment. The authors are thankful for the financial support by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 563/TP B7: "Bioorganic Functional Systems on Solids"). R.J. obtained additional financial support from the Graduiertenkolleg "Chemistry and Physics of Supramolecular Systems", by the Deutsche Akademische Austauschdienst (PROCOPE program), and by the Dr. Hermann-Schnell-Stiftung (GDCh).

References and Notes

(1) (a) Halperin, A.; Tirell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31 and references therein. (b) Sanchez, I. C. *Physics of Polymer Surfaces and Interfaces*; Butterworth: London, 1992 and references therein. (c) Zao, B.; Brittain, W. J. *Prog. Polym. Sci.* **2000**, *25*, 677 and references therein.
(2) Jordan, R.; Ulman, A. *J. Am. Chem. Soc.* **1998**, *120*, 243.
(3) Jordan, R.; Ulman, A.; Kang, J. F.; Rafailovich, M.; Sokolov, J. *J. Am. Chem. Soc.* **1999**, *121*, 1016.
(4) Jordan, R.; West, N.; Ulman, A.; Chou, Y.-M.; Nuyken, O. *Macromolecules* **2001**, *34*, 1606.
(5) Jordan, R.; Graf, K.; Riegler, H.; Unger, K. K. *Chem. Commun.* **1996**, *9*, 1025.
(6) Jordan, R. PhD Thesis, Johannes Gutenberg Universität Mainz, Mainz, 1996.
(7) Rehfeldt, F.; Tanaka, M.; Pagnoni, L.; Jordan, R., submitted for publication.
(8) (a) Velander, W. H.; Madurawe, R. D.; Subramanian, A.; Kumar, G.; Sinai-Zingde, G.; Riffle, J. S. *Biotechnol. Bioeng.* **1992**, *39*, 1024. (b) Woodle, M. C.; Engbers, C. M.; Zalipsky, S. *Bioconjugate Chem.* **1994**, *5*, 493. (c) Lasic, D. D.; Needham, D. *Chem. Rev.* **1995**, *95*, 2601. (d) Lehmann, T.; Rühe, J. *Macromol. Symp.* **1999**, *142*, 1. (e) Lehmann, T.; Rühe, J. *Macromol. Symp.* **1999**, *142*, 1.
(9) Bassiri, T. G.; Levy, A.; Litt, M. *J. Polym. Sci., Part B* **1967**, *5*, 871.
(10) Litt, M.; Rahl, F.; Roldan, L. G. *J. Polym. Sci., Part A-2* **1969**, *7*, 463.
(11) Loontjens, T.; Rique-Lurbet, L. *Des. Monomers Polym.* **1999**, *2*, 217.
(12) Seeliger, W.; Aufderhaar, E.; Diepers, W.; Feinauer, R.; Nehring, R.; Thier, W.; Hellmann, H. *Angew. Chem.* **1966**, *20*, 913.
(13) Ranganathan, N.; Storey, B. T. *J. Heterocycl. Chem.* **1980**, *17*, 1069.
(14) Kobayashi, S.; Masuda, E.; Shoda, D.; Shimano, Y. *Macromolecules* **1989**, *22*, 2878.
(15) Kobayashi, S.; Iijima, S.; Iijima, T.; Saegusa, T. *Macromolecules* **1987**, *20*, 1729.
(16) (a) Kuhn, P.; Weberskirch, R.; Nuyken, O.; Cevc, G. *Des. Monomers Polym.* **1998**, *1*, 327. (b) Kuhn, P.; Persigehl, P.; Jordan, R.; Nuyken, O., manuscript in preparation.
(17) Chujo, Y.; Ihara, E.; Ihara, H.; Saegusa, T. *Macromolecules* **1989**, *22*, 2040.
(18) Nuyken, O.; Maier, G.; Gross, A. *Macromol. Chem. Phys.* **1996**, *197*, 83.
(19) Cai, G.; Litt, M. *J. Polym. Chem. Ed.* **1992**, *30*, 649.
(20) Litt, M.; Levy, A.; Herz, J. *J. Macromol. Sci., Chem.* **1975**, *A9*, 703.
(21) Litt, M.; Hsieh, B. R.; Krieger, I. M.; Chen, T. T.; Lu, H. L. *J. Colloid Interface Sci.* **1987**, *115*, 312.
(22) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; Chapman and Hall: London, 1973.
(23) Angst, D. L. *Langmuir* **1991**, *7*, 2236.
(24) Snyder, R. G.; Strauss, H. L. *J. Phys. Chem.* **1982**, *86*, 5145.
(25) Rivas, B. L.; Ananias, S. I. *Polym. Bull.* **1992**, *28*, 3.
(26) Saegusa, T.; Yamada, A,; Taoda, H.; Kobayashi, S. *Macromolecules* **1978**, *11*, 435.
(27) Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145.
(28) Jordan, R.; Graf, K.; Simon, P.; Riegler, H.; manuscript in preparation.
(29) We considered the possible side products during the termination reaction arising by the kinetically controlled nucleophilic attack of the primary amine at the 2-position. This would create a hydroxyl-terminated polymer chain and *N*,*N*′-bis(2-ethyl)acetamidine. Numerical evaluation of the masses of these possible species does not fit to the values found in the mass spectra even considering different reaction pathways for products of an attack at the 2-position. However, the authors do not exclude this reaction pathway, but the total portion of side products belonging to the γ population calculates to about $<1-2\%$ and can therefore be neglected. The reaction of primary amines with the oxazolium end may be considered to be regioselective under the used reaction conditions.
(30) Since the total mass of the functionalized PPEI's is the sum of the mass of the monomer unit (ΔM) times the polymerization degree (n), plus the weight of the terminal functionalities and the attached ion(s) (residual mass RM), the actual polymerization degree which corresponds to the peak series in the mass spectra can be calculated by simple linear regression.
(31) Persigehl, P.; Jordan, R.; Nuyken, O. *Macromolecules* **2000**, *33*, 6977.

MA011573E