Nanocomposites by Surface-Initiated Living Cationic Polymerization of 2-Oxazolines on Functionalized Gold Nanoparticles

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ABSTRACT: End-functionalized 3D self-assembled monolayers (SAMs) on gold nanoparticles were used to initiate the living cationic ring-opening polymerization reaction directly on gold nanoparticle surfaces ("grafting-from technique"). In this manner, dense polymer brushes were prepared in a "one-pot multistep" reaction. ER FTIR spectroscopy confirms the successful polymerization reaction as well as the introduction of a terminal functional group. The resulting gold/polymer nanocomposite was very stable. The combination of a "grafting-from reaction" resulting in polymer "brush-type" shells of linear macromolecules and the introduction of a terminal mesogen by means of a quantitative termination reaction resulted in an amphiphilic core−shell material with a well-defined hydrophilic/lipophilic balance (HLB). Ex-situ kinetic studies of the polymerization of 2-phenyl-2-oxazoline using FTIR spectroscopy and MALDI TOF mass spectrometry resulted in a linear relationship between the reaction time and degree of polymerization of the grafted polymer. This as well as the successful end-functionalization by termination with secondary amines corroborates our view of a well-defined living polymerization mechanism.

Introduction

The preparation of nanocomposites with an inorganic core such as metal nanoparticles and a protective organic shell of small molar mass compounds or polymers is one route to obtain a material suitable for hierarchical self-organization into nanoassemblies.[1] The organic shell determines the chemical properties of such materials and their interaction with the environment, whereas their physical properties are determined by the size and shape of the metal core *and* the surrounding organic layer.[2]

Several research groups have successfully assembled functionalized particles into large nanocrystalline arrays using hydrophobic and electrostatic interactions, as well as chemical bridging.[3] Recently, we reported on the preparation and self-assembly of nanocomposites using selective electrostatic interactions intermediated by bola-amphiphilic bis(benzamidine)s.[4] Here we report on the preparation of gold nanoparticles surrounded by a shell of polymers of defined composition and morphology. The introduction of polymer shells in such nanoparticle materials opens the possibility to a broad range of multiple functional groups, e.g., block copolymers of known composition or end-functionalization.

The grafting of amphiphilic lipopolymer chains onto nanoparticles—resulting in a core−shell morphology with a hydrophilic inner and hydrophobic outer shell by means of a termination reaction of a hydrophilic polymer with a hydrophobic terminating agent—is especially intriguing. The particle−particle interactions and the organization into larger supramolecular arrays would then be directed via the hydrophobic effect. The synthetic pathway used to obtain such nanoparticles along with a schematic representation of the final material is depicted in Figure 1.

The coupling of preformed functionalized polymers onto the surface of nanoparticles with typical diameters of 2−5 nm would not result in a compact core−shell system for steric reasons. Therefore, to achieve a macromolecular design of a dense polymer shell, a "grafting-from" technique must be applied using a controlled surface-initiated polymerization such as "living" radical,[5] living ionic polymerization techniques, or ring-opening metathesis polymerization.[6]

Based on the synthetic concept we have developed for preparing dense polymer brushes on planar gold substrates,[7,8] 3D ω-functionalized self-assembled monolayers (SAM) of thiolates on gold nanoparticles were used to initiate living cationic ring-opening polymerization (see Figure 1). This report describes a series of analogue reactions conducted using 11-hydroxyundecane-1-thiol ($HO-(CH_2)_{11}-SH$, HUT)-functionalized gold nanoparticles as the starting material. When considering the size as well as the physicochemical properties of metal nanoparticles, they can be regarded as solid bulk substrates or as classical macroinitiators.

Experimental Section

Chemicals. Dry tetrahydrofuran (THF) and chloroform were received from EM Science, distilled under a nitrogen atmosphere, and stored over molecular sieves (4A). Trifluoromethanesulfonic anhydride, 1.0 M THF solution of lithium triethylborohydride (Aldrich), tetrachloroaureate(III) trihydrate (Aldrich), trifluoromethanesulfonic anhydride (Aldrich), and *N*,*N*-di-*n*-octadecylamine (Fluka) were used as received. 2-Ethyl-2-oxazoline (Aldrich) was purified by refluxing (2 h) over KOH and a subsequent distillation under a dry nitrogen atmosphere. Piperidine (Aldrich) was distilled and dried prior to use. 2-Phenyl-2-oxazoline was prepared according to Seeliger and co-workers[9] from freshly distilled aminoethanol (Aldrich) and benzonitrile (Aldrich), using a 1:1 molar ratio and $Zn(CH_3COO)_2 \cdot 2H_2O$ as the catalyst (0.0125 mol/1 mol nitrile), and

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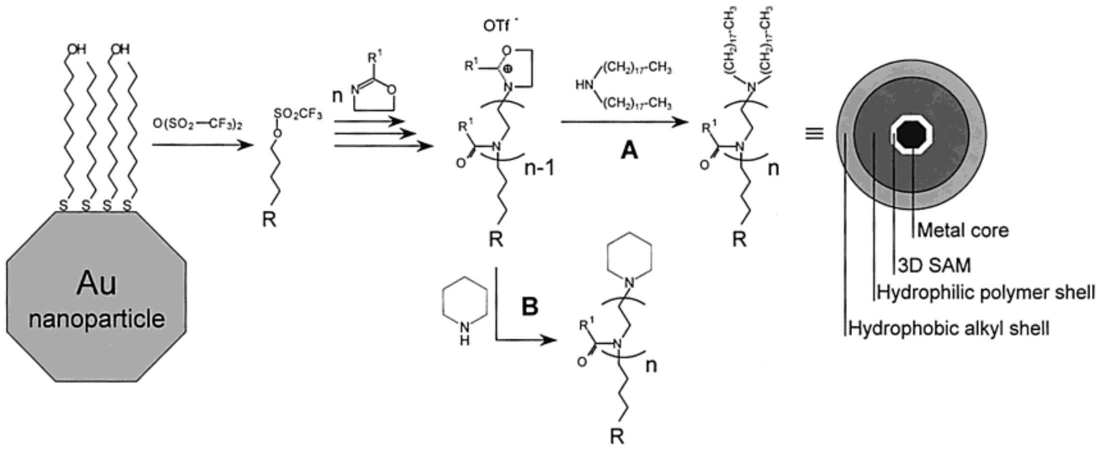

A (amphiphilic core-shell): $R^1=C_2H_5$-; Terminating agent: *N,N*-di-*n*-octadecylamine; polymerization time: 72h

B (*ex situ* kinetics): $R^1=C_6H_5$-; Terminating agent: piperidine; polymerization time: 2, 8, 24, 79h

Figure 1. Reaction scheme of the surface-initiated polymerization of 2-oxazolines: For the preparation of the amphiphilic nanocomposite 2-ethyl-2-oxazoline and *N*,*N*-di-*n*-octadecylamine were used as monomer and terminating agent, respectively (pathway A). The kinetic studies were performed with 2-phenyl-2-oxazoline and piperidine. A schematic representation of the core−shell morphology of the amphiphilic metal−polymer composite.

purified by refluxing (2 h) over KOH and distillation under a dry nitrogen atmosphere.[10]

Preparation of HUT-Functionalized Gold Nanoparticles. Thiolate-functionalized gold nanoparticles were prepared using a novel one-phase synthesis as previously published.[11] In short, 1 mM alkanethiol (0.1 mM HUT and 0.9 mM *n*-undecanethiol, C_{11}) in 1 mL of THF was added under vigorous stirring to a solution of 1 mM tetrachloroaureate(III) trihydrate in 10 mL of THF in a 100 mL vessel. After further stirring at room temperature for 30 min, a 1.0 M THF solution of lithium triethylborohydride was added dropwise under efficient cooling (T = 20−25 °C), until no more gas evolution was observed. The product was isolated by centrifugation and washed excessively with freshly distilled THF. Both particle size and particle size distribution, as determined by transmission electron microscopy, and the functionalization with the 3D SAM, as determined by FTIR spectroscopy, were in all cases in full agreement with results reported before, with an average particle diameter of 4 nm.[11]

Surface-Initiated Polymerization of 2-Substituted-2-Oxazolines. The polymerization reaction was carried out following the general procedure for the preparation of poly(2-oxazoline) brushes on planar 2D-SAMs.[7] However, slight modifications of the preparation were necessary: 0.5 g of freshly prepared, washed (THF), and dried C_{11}/HUT-modified particles was transferred into a 200 mL reaction vessel equipped with a condenser and a three-way stopcock. The air was exchanged with dry nitrogen gas by repetitive evacuation (6−7 cycles) and purging with dry nitrogen. The powder was exposed to a constant trifluoromethanesulfonic anhydride vapor/nitrogen stream for about 1 h. The conversion of the HUT hydroxyl groups to the triflate functional group was allowed to complete overnight in the sealed reaction vessel. The reactor was again evacuated and left under high vacuum for approximately 4 h to remove any excess of the anhydride or acid and then purged with dry nitrogen. Using airtight syringes and septa, 20 mL of dry chloroform and 5 mL of freshly distilled 2-ethyl-2-oxazoline (pathway A in Figure 1) or 2-phenyl-2-oxazoline (pathway B) were added at 0 °C under vigorous stirring. The reaction mixture was then heated by an oil bath and allowed to react under reflux conditions for up to 3 days. The polymerization was terminated by adding a solution of 0.1 g of *N*,*N*-di-*n*-octadecylamine in 2 mL of dry chloroform or 2 mL of piperidine (for poly(2-ethyl-2-oxazoline)) at 0 °C. For the ex-situ kinetic studies (pathway A), portions of the polymerization solutions were taken out (2.5 mL after 2 h; 3 mL after 4 h; 5 mL after 8, 24, and 79 h) and added to 2 mL of piperidine. The crude product was isolated (precipitation $CHCl_3$/ether), filtered, and washed excessively with $CHCl_3$ to separate the nanocomposite material from the pure polymer. Both fractions were again reprecipitated and freeze-dried (benzene) for further analysis.

Decomposition of the Polymer/Gold (PG) Nanocomposite Using NaCN.[12] The nanocomposite (10 mg) were suspended in 1 mL of freshly distilled acetonitrile and approximately 20 mL of water. To this suspension was added 10 mg of NaCN. The mixture was stirred for 16 h or until the violet color completely disappeared, indicating the decomposition of the metal core. The solvent mixture was then carefully removed, and the crude product was extracted with 30 mL of freshly distilled chloroform. Mass spectrometry was performed from the isolated polymer solution without further purification.

FTIR Spectroscopy. The external reflection infrared (ER-FTIR) spectra were recorded using a Magna 760 IR spectrometer (Nicolet) equipped with a grazing angle setup (fixed angle of 80°, FT-80, SpectraTech), a polarizer (p-polarization), and a MCT-A detector cooled with liquid nitrogen; 2000 scans were accumulated at a 2 cm^{-1} resolution. The spectra of the HUT-functionalized gold nanoparticles and the bulk polymer as well as the PG nanocomposites were recorded on the same spectrometer in transition mode (KBr pellet) at a 2 cm^{-1} spectral resolution (500 scans).

MALDI TOF Mass Spectrometry. Mass measurements were performed using a Bruker BIFLEX III MALDI TOF mass spectrometer equipped with a nitrogen laser (LSI, 337 nm, 3 ns pulse length) and two detectors. For external calibration poly(ethylene glycol) standards were used. The laser power was adjusted slightly above the threshold (10^6−10^7 W/cm^2). The ions were accelerated by a potential of 19 kV and reflected with a 20 kV potential. For each spectrum, approximately 100 transients were accumulated. All spectra were recorded in the reflection mode, using a double plate microchannel detector at the end of the second flight tube. Because of the better signal-to-noise ratio, only reflection spectra are presented here as used for the data evaluation (Bruker XMASS program). 1,8,9-Trihydroxyanthracene (Aldrich) was found to be a suitable matrix. It was dissolved in chloroform and mixed with the sample in the same solvent. Finally, 5 μL of a $LiCF_3CO_2$ solution (c = 1 g/L) was added and stirred shortly. The addition of a small amount of a lithium salt was found to ensure a selective and quantitative ionization of the sample molecules. A fraction of 1 μL of the final mixture was placed on the multistage target, air-dried, and transferred into the mass spectrometer.

Results and Discussion

The preparation of stabilized metal nanoparticles of controlled size can be achieved following the classical preparation route by reduction of metal salts in the presence of alkanethiols as developed by Brust and coworkers.[13] However, this two-phase preparation technique was unsuitable when ω-functionalized alkanethiols must be used for the preparation of functionalized gold nanoparticles. We recently developed a novel route for a facile preparation of metal nanoparticles bearing various surface functional groups.[11] This route is especially suitable for the preparation of uncontaminated nanoparticle material due to the surfactant-free conditions and facile workup procedure by simple filtration and washing with THF in which all side products are soluble. The preparation of HUT-modified gold nanoparticles was performed as described before; the properties of the resulting material in terms of particle size, size distribution, and functionality were as reported.[13] The conversion of the terminal hydroxyl group into the triflate group was carried out in the gas phase using a medium stream of trifluoromethanesulfonic anhydride (($CF_3-SO_2)_2O$). Analogue reaction conditions on 2D-HUT SAMs on planar gold substrates were used.[7] The gas-phase reaction ensures good conversion of the OH groups, and no removal of a solvent or further cleaning procedures are necessary. However, due to the water sensitivity of the triflate groups, no spectroscopic investigations of the activated nanoparticles were performed, and the yield of this reaction is unknown. The resulting surface-bonded triflate SAM is a highly efficient initiator for the cationic ring-opening polymerization of 2-alkyl-2-oxazolines.[14] First, triflate is a better leaving group than the commonly used tosylate initiator ($k_{\text{initiation}} \gg k_{\text{propagation}}$); second, the triflate gegenion ensures a strictly ionic mechanism of the propagation reaction.[15] This ensures a living and stoichiometric polymerization. In this particular study, a mixed 3D SAM system of n-undecanethiol and HUT (10:1 C_{11}:HUT) was used in order to avoid overcrowding of the nanoparticle surface during the initiation step.

For the termination reaction, nucleophiles such as primary or secondary amines are suitable.[16] In this paper, two different termination agents were used. *N*,*N*-Di-*n*-octadecylamine was used for the termination of the hydrophilic poly(2-ethyl-2-oxazoline) to prepare an amphiphilic lipopolymer shell around the gold core (compare Figure 1 pathway A). An excess of piperidine, a highly effective termination agent, was used for the kinetic studies of the grafting polymerization of poly(2-phenyl-2-oxazoline) (pathway B).[16]

In contrast to our previous experiments on surface-initiated living cationic polymerization of 2-oxazolines on planar substrates,[7] the progression of the living polymerization can be followed ex situ by standard analytical methods such as MALDI-TOF mass spectrometry and transmission FTIR spectroscopy. Functionalization via the termination reaction should be clearly observable by these analytical methods.

In this context, it is noteworthy that the "grafting from" polymerization using flat surfaces (2D SAMs) and nanometer sized cores as substrates (3D SAMs) differs significantly due to the extreme difference in the surface curvature of the substrates. Surface crowding will have a different impact during the initiation reaction as well as during the growth of the polymer chains. However, using high surface area material, e.g., silica gel or as in this case gold nanoparticles, proved to give further insights into surface-initiated polymerization reactions.[17]

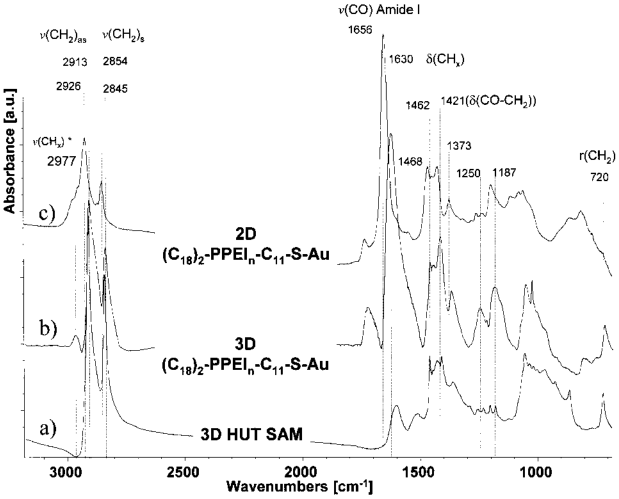

Figure 2. Transmission FTIR spectra of the (a) starting material C_{11}/HUT on gold nanoparticles and (b) the obtained metal–polymer nanocomposite. For comparison, an ERFTIR spectrum of a freshly prepared poly(2-ethyl-2-oxazoline) brush ($d = 17$ nm) bearing the same functionalities is also presented (c) ($\nu(CH_x)^*$ modes of $-C_2H_5-CO-$ and $-CH_2-N-$ of the polymer backbone).

Amphiphilic Core–Shell Nanocomposites by the "One-Pot MultiStage Technique". The successful preparation of the amphiphilic core–shell nanocomposite was confirmed by FTIR spectroscopy (Figure 2). The transmission FTIR spectrum of the final product is displayed along with the spectra of the HUT/C_{11}-modified nanoparticles for comparison and an ER FTIR spectrum of poly(2-ethyl-oxazoline) brush prepared on a planar HUT/C_{11} SAM, end-functionalized with the same terminating agent (b-PPEI-C_{18}).[18] The similarity of spectra b and c and a comparison with a typical bulk spectrum of poly(2-ethyl-2-oxazoline) confirm a successful polymerization reaction.[19]

Typical features of the polymer spectrum are the appearance of the strong amide I band (1656, 1630 cm^{-1}), the characteristic stretching vibrational modes of the methylene groups in the polymer backbone, and the propionyl side chain around 2977 cm^{-1}, as well as their deformation modes at 1421 cm^{-1}.[20] All of these bands are absent in spectrum a. The presumably complete conversion of the terminal hydroxyl function of the HUT particles to the triflate initiator was confirmed by the disappearance of the broad ν(OH) stretching mode centered around 3570 cm^{-1}. A successful end-functionalization of the grafted polymer chains by long n-alkyl moieties is indicated by the appearance of strong symmetric and asymmetric CH_2 stretching modes. While the $\nu(CH_2)$ stretching modes for the 2D polymer brush are centered at 2926 (ν_{as}) and 2854 cm^{-1}, the same mode has its band maximum at 2913 and 2845 cm^{-1} for the 3D core–shell system. The significant lower band maxima are typical for long n-alkyls associated in an all-trans configuration[21] and can be explained by an interparticle or most probably intraparticle crystallization of the terminal octadecyl chains. Consequently, a picture arises where the core–shell nanoparticles are forming a 3D assembly associated via the alkyl moieties and spaced by the inner polymer core. This association has been observed on n-alkanethiolate-modified nano-

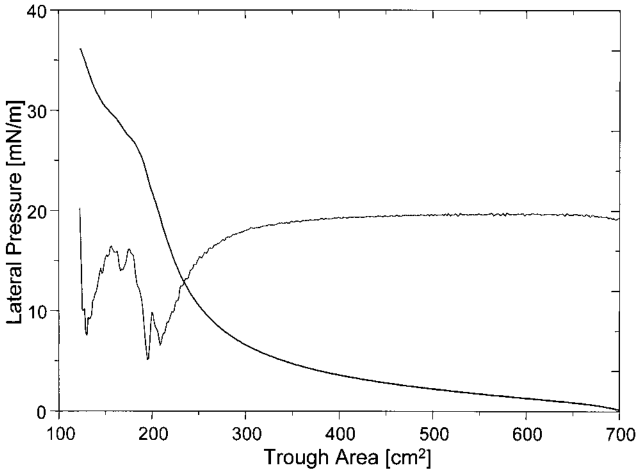

Figure 3. $\Pi-A$ isotherm of the amphiphilic nanocomposite (T = 23 °C) and its derivative. The monolayer was prepared by spreading a dilute dispersion ($CHCl_3$) on a clean water surface of a LB trough (LAUDA). Multiple compression/expansion cycles at low speeds (2 mm^2/s) gave no significant change of the isotherms. Faster compressions resulted in the formation of visible multilayers of the particles. A formation of larger agglomerates accompanied by a significant pressure drop was observed when the particle monolayer was left for several hours at high initial pressures.

particles.[22] However, both the interparticle crystallization and the intraparticle association of alkyl chain bundles were discussed but could not be clarified. Because of the higher steric restriction for the association of the alkyl chains into all-trans domains, the polymer tethered *n*-octadecyl chains seem to arrange into larger arrays with less gauche defects. Unfortunately, a more detailed analysis based on the present spectra is not possible because of overlapping bands originating from the polymer alkyl groups. The surface confinement of the poly(2-ethyl-2-oxazoline), grafted to the particle and bonded via the terminal alkyl moiety, is reflected by a significant shift of the amide I band maximum to lower wavenumbers (1656 cm^{-1} for the 2D brush of PPEI-C_{18}, 1630 cm^{-1} for the polymer nanoparticles in bulk).

The amphiphilic nature of the nanocomposite allowed the preparation of stable Langmuir layers at the air–water interface (Figure 3). The pressure–area ($\Pi-A$) isotherm displayed a long and slow increase of the surface pressure, typical for the compression of amphiphilic poly(2-oxazoline) lipopolymers, followed by a sharp increase of the lateral pressure upon compression (from 5 to 25 mN/m) and a change in the slope around 27.4 mN/m followed by numerous changes in the slope at higher pressures (see displayed derivative of the $\Pi-A$ isotherm in Figure 3). However, the $\Pi-A$ isotherm of the amphiphilic nanoparticles does not show the compression-induced plateau at intermediate surface pressures which originates from the desorption of the slightly amphiphilic poly(2-ethyl-2-oxazoline) segment from the air–water interface.[23] This can be explained by the tethering of the polymer to the nanoparticles. The nature of the numerous changes in the slope of the isotherm and the morphology of the nanoparticle monolayer at different pressures will be the subject of further studies.

Ex-Situ Kinetic Studies. 2-Phenyl-2-oxazoline was chosen as the monomer for ex-situ kinetic studies,[24] using the same starting triflate-modified nanoparticles. Fractions of the reaction solution were collected at 2, 8, 24, and 79 h and transferred under inert conditions into an excess of dry piperidine. After completion of the termination reaction and careful workup of each fraction, the samples were investigated by transmission FTIR spectroscopy. The amide I region of the obtained spectra is displayed in Figure 4.

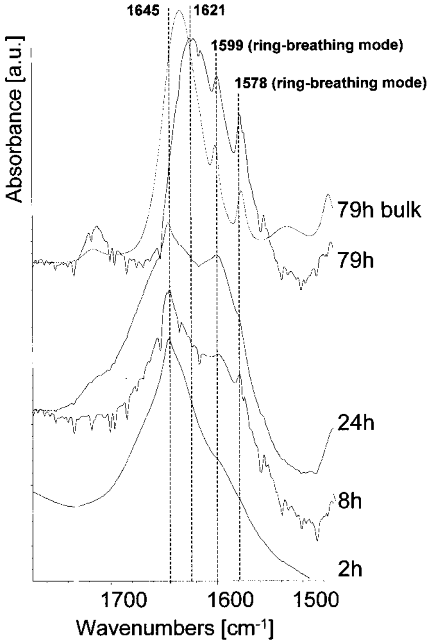

Figure 4. Amide I band region of the FTIR transmission spectra of the poly(2-phenyl-2-oxazoline)/metal composite after the indicated reaction times. For comparison, a spectrum of the pure polymer, which was isolated after 79 h from the reaction solution, is displayed. The formation of unbounded polymer was always observed. This is due to an incomplete removal of trifluoromethanesulfonic acid. Previous experiments showed that a complete removal can be realized; however, layer thickness and quality of 2D brushes are better when small amounts of an initiator remain in the reaction system in order to capture impurities.

The increase of the polymer chain length of the tethered polymer is qualitatively indicated by the increase of the integral absorption intensity of the amide I band relative to the alkyl stretching bands originating from the C_{11}/HUT 3D monolayer (not shown). The amide I band maximum shifts from 1645 cm^{-1} for short chains to 1621 cm^{-1} for longer chains after a polymerization time of 79 h, with further bands at 1599, 1578, 1493, and 1462 cm^{-1} originating from the ring-breathing modes of the aromatic ring.

MALDI TOF Mass Spectrometry. Following a procedure previously published by Tempelton and coworkers,[12] the obtained fractions of the nanocomposites were decomposed using NaCN to liberate the tethered polymers and analyze the degree of polymerization as a function of the reaction time by mass spectrometry. The mass spectrum of the 2 h fraction (Figure 5) features one prominent series of mass signals with a ΔM = 146.93, which is in good agreement with the calculated mass of a poly(2-phenyl-2-oxazoline) monomer unit of M = 147.17, and are thus mass signals of the polymer with the same end groups. As reported by Tempelton and co-workers,[12] the detected liberated species should feature a dialkyl disulfide group at one end and a piperidine function at the other chain terminus. Because of the ratio of the original mixed 3D SAM of alkanethiols (C_{11}:HUT, 10:1) on the gold nanoparticles, the most probable product of the decomposi-

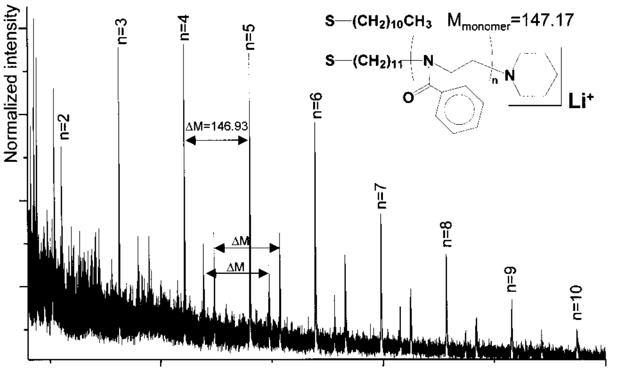

Figure 5. Normalized MALDI TOF mass spectrum of the first fraction (2 h) of poly(2-phenyl-2-oxazoline) isolated by dissolving the gold core with NaCN solution. The calculated mass of the monomer unit (147.17) is in good agreement with the spacing of the mass signals (ΔM = 146.93) of the most prominent peaks. On the basis of earlier findings by Tempelton and co-workers, the species of the isolated polymer were assumed to have an asymmetric dialkyl disulfide structure.

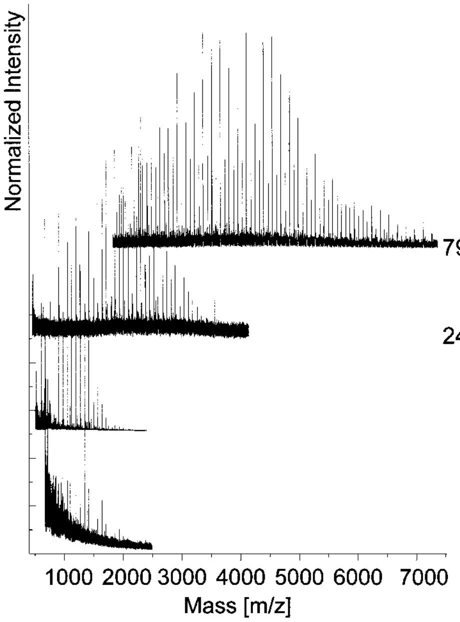

Figure 6. Normalized MALDI TOF spectra of all isolated fractions of poly(2-phenyl-2-oxazoline). Spectra are shifted along the *y*-axis for clarity.

tion reaction should bear an asymmetric dialkyl disulfide as displayed in Figure 5.

Indeed, the calculated mass of this compound matches the total mass of the polymer/Li^+ with $n = 3$ (m/z = 906.63; $M_{\text{calculated}} = 906.37$). There are two minor series of signals, besides the main population, with a ΔM of the monomer unit. Although an unambiguous identification was not possible, the relative intensity of these signals changed for repeated decomposition reactions and are therefore most probably products formed by this reaction. Figure 6 lists all MALDI TOF mass spectra with increasing polymerization time. The number-average degree of polymerization increases steadily with a slight broadening of the molecular weight distribution.[25] Plotting the m/z value of the most intensive mass signal vs the reaction time, a strictly linear relationship is obtained (Figure 7). These results are consistent with recent experimental and theoretical studies of surface-initiated atom transfer radical polymerization (ATRP) by Matyjazsewski and co-workers.[5] The initiation reaction by the alkyltriflate seems to be much faster than the propagation reaction, which is indicated by the significantly steeper slope between $t = 0$ and 2 h. This means that the induction period of the polymerization is not noticeably hindered by the surface confinement of the initiator. From this, as well as from the successful termination reaction with secondary amines, we conclude that the surface-initiated cationic ring-opening polymerization of 2-oxazolines with alkyl triflate as the initiator is of living character.

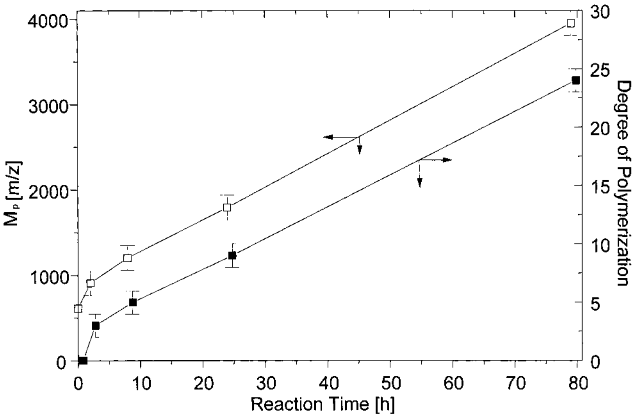

Figure 7. Plot of the most intensive mass signal (M_p) vs reaction time. The corresponding degree of polymerization was calculated on the basis of the identified species as depicted in Figure 5.

Conclusions

Functionalized metal nanoparticles can be used as starting materials for living cationic polymerization reactions. Complex core−shell morphologies of amphiphilic nanocomposites were obtained by a "one-pot multistage" reaction. Using appropriate initiators and 2-oxazoline monomers, the ring-opening polymerization progresses in a living manner. The presented work can be applied to a wide range of 3D SAM/metal particle systems for the polymerization of various 2-substituted 2-oxazoline monomers to allow the preparation of new functional composites at the nanometer scale.

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(19) The formation of the polymer of 2-ethyl-2-oxazoline by ring-opening polymerization can unambiguously be identified by the presence of the strong amide I band around 1640 cm^{-1} originating from the amide group in the polymer backbone. A typical bulk spectrum of poly(2-ethyl-2-oxazoline) is given in ref 7.

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