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

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Received September 19, 2000

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 confirmed 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. 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.

Several research groups have successfully assembled functionalized particles into large nanocrystalline arrays using hydrophobic and electrostatic interactions, as well as chemical bridging. Recently, we reported on the preparation and self-assembly of nanocomposites using selective electrostatic interactions intermediated by bola-amphiphilic bis(benzamidines). 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 macro-molecular design of a dense polymer shell, a "grafting-from" technique must be applied using a controlled surface-initiated polymerization such as "living" radical, living ionic polymerization techniques, or ring-opening metathesis polymerization.

Based on the synthetic concept we have developed for preparing dense polymer brushes on planar gold substrates, we 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–(CH2)10–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 Seifler and co-workers from freshly distilled aminoethanol (Aldrich) and benzonitrile (Aldrich), using a 1:1 molar ratio and Zn(CH3COO)2·2H2O as the catalyst (0.0125 mol/1 mol nitrile), and...
core

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 pub-

lished.11 In short, 1 mM alkanethiol (0.1 mM HUT and 0.9

mM n-undecanethiol, C11) 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

evaporation was observed. The product was isolated by cen-

trifugation 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 C11/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

evapor/nitrogen stream for about 1 h. The conversion of the

HUT hydroxyl groups to the triflate functional group was

achieved slightly above the threshold (10 6

10 7 W/cm2). 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).

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 (106–107

W/cm2). 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).
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 co-workers. However, this two-phase preparation technique was unsuitable when α-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. 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.

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 (CF3SO2O). Analogue reaction conditions on 2D-HUT SAMs on planar gold substrates were used. 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. First, triflate is a better leaving group than the commonly used tosylate initiator; second, the triflate gegenion ensures a strictly ionic mechanism of the propagation reaction. This ensures a living and stoichiometric polymerization. In this particular study, a mixed 3D SAM system of n-undecanethiol and HUT (10:1 C11: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. 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).

In contrast to our previous experiments on surface-initiated living cationic polymerization of 2-oxazolines on planar substrates, 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.

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/C11-modified nanoparticles for comparison and an ER FTIR spectrum of poly(2-ethyl-2-oxazoline) brush (d = 17 nm) bearing the same functionalities is also presented. The 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. 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 (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 CH2 stretching modes. While the (CH2) stretching modes for the 2D polymer brush are centered at 2926 (vas) 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 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-
particles. 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 (II–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 II–A isotherm in Figure 3). However, the II–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. 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, 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.

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 co-workers, 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 \(\Delta M = 146.93\), 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, the detected liberation 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-
of signals, besides the main population, with a slight broadening of the molecular weight distribution. Plotting the average degree of polymerization increases steadily with increasing polymerization time. The number-reaction. Figure 6 lists all MALDI TOF mass spectra and are therefore most probably products formed by this reaction. 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. 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. Ploting 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) functional composites at the nanometer scale.

**Acknowledgment.** Funding from the NSF MRSEC for Polymers at Engineered Interfaces is gratefully acknowledged. R.J. is thankful for financial support from the Gesellschaft Deutscher Chemiker e.V. in the form of the Dr. Hermann Schnell stipend, the Fonds der Chemischen Industrie (FCI), and the Deutsche Forschungsgemeinschaft (SFB 563 ‘Bioorganische Funktionssysteme an Festkörperoberflächen’). A.U. thanks the Alexander von Humboldt Foundation for supporting his stay in Germany.

**References and Notes**

Polymerization of 2-Oxazolines


(18) The 2D (C18)2-PPEI-C11-Au brush was prepared according to ref 7. The dry thickness of the polymer brush was 17 nm (measured by ellipsometry). AFM studies confirmed a uniform layer morphology.

(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.


(24) 2-Phenyl-2-oxazoline was used to investigate the “livingness” of the surface-initiated polymerization because of the absence of a possible transfer reaction at long polymerization times (see: Cai, G.; Litt, M. J. Polym. Chem. Ed. 1992, 30, 649).

(25) A quantitative analysis and determination of the polydispersity index based on the mass spectra is not given due to observed discrimination of low or higher masses by the ionization with lithium or potassium, and the necessary setting of a signal cutoff ranged from 500 to 1500 depending on the measurement. Analysis of elution traces using gel permeation chromatography failed.