Metal Salt Complexation of Spin-Coated Ultrathin Diazosulfonate Terpolymer Films

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Received August 9, 2001

ABSTRACT: We report the successful metal salt complexation of ultrathin terpolymer films spin-coated onto glass and silicon substrates as well as the subsequent reduction of the salt to metal clusters. The photolabile polymer consists of a diazosulfonate side chain polymer which may be decomposed under UV irradiation. All stages, i.e., initial, complexed, and reduced stage, are characterized using optical transmission spectroscopy and X-ray photoelectron spectroscopy. The film surface roughness, morphology, and thickness are determined by atomic force microscopy and ellipsometry. On one hand, our experiments show that nonirradiated diazosulfonate side groups complex with silver acetate provided from solution and that silver ions chemically reduce when exposed to a sodium borohydride solution. On the other hand, the complete destruction of the photolabile diazosulfonate unit under UV irradiation is proven. Our experimental investigations are the first successful efforts demonstrating the selective metallization of deposited ultrathin diazosulfonate polymer films.

Introduction

Today, metallization and surface finishing are important fields of applications in our macroscopic world as well as in nanotechnology.[1] Conventional methods for the deposition of metallic conducting films use the galvano technique; however, this technique is limited to conducting surfaces or surfaces treated with a conducting precursor film. Furthermore, not every metal is suited for a proper deposition.[2] Additionally, the spatially defined structuring of the metal surface is only possible via a subsequent process step and requires great expenditure.

Alternatively, the use of template polymers offers possibilities for the defined positioning of metal clusters. Segregation phenomena in di- and triblock copolymers can form controlled surface structures due to phase separation in thin films, and in given compositions such polymers can incline to form micelles.[3−9] The micelle formation especially studied on block copolymers with poly(2-vinylpyridine) segments loaded with silver or gold salts can assist the formation and deposition of uniform metal particles with a diameter of 1−12 nm in quasi-hexagonal grid structures having a pitch of 20−200 nm on planar substrates. The "template polymers" have been removed by plasma etching processes after reduction of the embedded metal salts.[10−16] In this way, the defined synthesis and attachment of Co, Fe, Pd, Pt, and Ru colloids on surfaces were realized,[11] and the principle has already been applied in the field of nanolithography for example by Chaikin[17] and Spatz,[18] who succeeded to structure SiN or GaAs substrates with holes or islands in the range down to 20 nm.

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However, the use of template polymers usually results in metal structures or clusters in a given order and dimension as predetermined by the polymer phase morphology. The achievement of irregular but defined metal structures on surfaces therefore is still a challenge.

An alternative to template techniques is provided by procedures that generate structured functional surfaces in advance to the metal salt complexation. Generally, optical lithography using UV irradiation with or without a mask can be applied for the spatially defined structuring of photosensitive surfaces or polymer films. Novel methods for surface structuring on the nanometer scale using no mask are available by the use of laser writing technologies such as scanning near-field optical microscopy (SNOM).[19−24]

Our experiences with polymer films containing the photolabile diazosulfonate[25−27] and with the property of the sulfonate group to complex oppositely charged organic compounds[28−30] or metal salts[31,32] render these substances a promising candidate for the selective complexation of metal salts after lithographic structuring.[33]

In this paper, we report the use of a photoaddressable diazosulfonate terpolymer film, covalently attached on glass or silicon substrates as the template surface for the selective complexation of silver salts and the subsequent reduction of the salt to silver clusters. The metal salt complexation is achieved by counterion exchange of the diazosulfonate group from Na^+ to for example Ag^+.

Experimental Part

Polymer Synthesis. The investigated photolabile terpolymer was synthesized from the three monomers: methyl methacrylate (MMA), sodium 4-acryloylaminophenyldiazosulfonate (APAS), and 3-(trimethoxysilyl)propyl methacrylate (TMSPMA).[34] The chemical structures of all components are shown in Figure 1. MMA is used as a spacer molecule, the siloxane unit provides covalent bonding to the glass or silicon substrate, and the phenyldiazosulfonate unit is the photolabile

10.1021/ma0114335 CCC: $22.00
Published on Web 01/29/2002

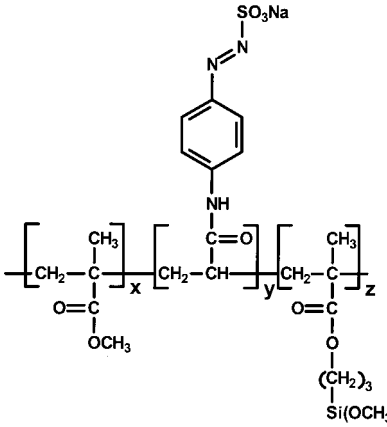

Figure 1. Chemical structure of the synthesized terpolymer methyl methacrylate (MMA)/sodium 4-acryloyl-aminophenyl-diazosulfonate (APAS)/3-(trimethoxysilyl)propyl methacrylate (TMSPMA). The molar ratio of the three monomers is MMA x = 75%, APAS y = 20%, and TMSPMA z = 5%.

part. APAS was synthesized according to the literature[26] while the other two constituents were purchased from Fluka. All solvents used were purified and dried. Reaction and purification were performed under nitrogen gas in a flame-dried apparatus. The terpolymer (molar ratio of the three monomers MMA 75%, APAS 20%, TMSPMA 5%) was synthesized by radical polymerization of the three monomers in DMSO with azobis(isobutyronitrile) initiator: 0.3755 g (3.75 mmol) of MMA, 0.2770 g (1.0 mmol) of APAS, and 0.0620 g (0.25 mmol) of TMSPMA were dissolved in 7 mL of DMSO-d_6, and 0.041 g of AIBN (0.25 mmol) was added. The polymerization was carried out at 70 °C for 20 h. When the reaction had stopped, the solvent was removed in a vacuum, and the terpolymer was dissolved in methanol. The solution then was added drop by drop to ice-cooled diethyl ether in order to purify the polymer. The resulting precipitate was filtered and dried in a vacuum. The terpolymer was obtained in quantitative yield.

^{1}H NMR (DMSO-d_6): δ = 0.4−0.6 ppm (−CH_2−Si−), 0.6−2.1 ppm (−CH_2−, −CH_3, polymer chain), 3.4−3.55 ppm (−OCH_3, Si$(OCH_3)_3$), 3.8−3.9 ppm (−O−CH_2−), 7.7−7.8 ppm (Ar−H), 10.0−10.2 ppm (−NH−)].

IR-ATR (film): ν (cm^{-1}) = 3330 (N−H), 2800−3000 (C−H), 1730 (C=O), 1600 (C=C, aromatic), 1510 (CONH), 1245 (−SO_3^-, wide).

UV/vis (film): λ_{max} = 336 nm (−N=N−SO_3^-); (solution, DMSO): λ_{max} = 323 nm (−N=N−SO_3^-).

Thin Film Preparation. Thin polymer films were prepared on cleaned glass substrates (Menzel Glasbearbeitungswerk GmbH & Co. KG, D-38021 Braunschweig, Germany) or silicon wafers (Orientation 100, p-doped, 50 nm SiO_2 layer). Substrates were first sonicated for 10 min in acetone followed by 10 min in a "piranha" solution (75% concentrated H_2SO_4, 25% concentrated H_2O_2), rinsed several times in Millipore water, and dried in nitrogen. Spin-coating was carried out from a 1 wt % methanol solution of the terpolymer by using a photoresist spinner (Headway Research Inc., Garland, TX). Films were then annealed for 30 min to 80 °C in a water-saturated atmosphere, followed by a 2 h exposure at 120 °C to atmospheric pressure. The films investigated were spin-coated at 3000 rpm, which results in films of about 20 nm thickness with less than 1 nm roughness (rms). The film thickness was determined both using a variable angle multi-wavelength ellipsometer (A.J.A. Wollam Co. M44, Inc., Lincoln, NE) and an atomic force microscope[35] (AFM, ThermoMicroscopes Explorer, Sunnyvale, CA). For the first method, a 75 W xenon arc lamp was used for illuminating polymer-coated Si (100) wafers with 50 nm SiO_2 at 22 °C and 40% humidity measuring at three different angles between 65° and 75°. AFM was used to determine the film thickness on glass substrates by scratching the terpolymer film and analyzing the height difference between substrate and film within the resulting scratch structure. These results on glass were comparable to ellipsometry measurements on silicon substrates.

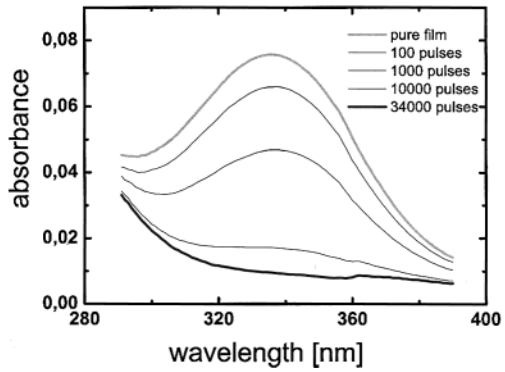

Figure 2. Optical absorbance as a function of decomposed diazosulfonate groups displayed after several amounts of UV laser pulses. Each laser pulse at λ = 337.1 nm has an energy of ∼130 μJ focused onto an area of 4 mm × 5 mm. Note the dramatic peak reduction at λ ∼ 336 nm.

UV Exposure. UV laser illumination was performed with a pulsed nitrogen laser (LTB Lasertechnik Berlin GmbH, MSG 350-SD, pulse length τ = 500 ps, pulse rate ∼ 20 Hz, wavelength λ = 337.1 nm). Each laser pulse has an energy of ∼130 μJ, which is then focused onto the investigated sample area. The total energy of the 50 000 pulses used to crack all diazosulfonate groups of the illuminated area corresponds to a total energy of ∼6.5 J.

Complexation. The sodium counterions of the above-described films were exchanged by silver ions by immersing the samples for 2 h in a 0.01 M solution of Ag(CH_3COO) in water (silver acetate was purchased from Fluka). After the complexation, the samples were rinsed and sonicated several times in Millipore water, dried in a nitrogen stream, and annealed for 30 min to 80 °C in a vacuum.

Reduction. Chemical reduction was obtained by immersing the silver salt complexed films for 10 min in a solution of sodium borohydride ($NaBH_4$, purchased from Fluka) in water. These samples were sonicated in Millipore water as well, dried in nitrogen, and annealed for 30 min to 80 °C in a vacuum.

Optical Spectroscopy. The optical properties of the photolabile terpolymer thin films on glass were analyzed measuring the optical transmission with a Shimadzu UV 3100 UV−vis−NIR recording spectrophotometer. All displayed data show relative absorption changes in comparison to clean glass substrates. For these measurements the investigated sample area was 4 mm × 5 mm in size.

XPS. X-ray photoelectron spectroscopy (XPS) data were acquired with a Leybold EA 10 energy analyzer and a Mg-anode X-ray source under ultrahigh-vacuum conditions with a pressure of $<10^{-9}$ mbar. The investigated sample area measured 0.5 mm × 10 mm.

Results and Discussion

Copolymers of a diazosulfonate monomer and for example methyl methacrylate have been studied previously as photoresins for the preparation of offset printing plates using UV light and a mask as well as IR lasers for lithographic structuring.[25−27] UV illumination modifies the structure of the diazosulfonate group.

The polar diazosulfonate groups decompose under nitrogen evolution. In water solution mainly phenol groups result, but the photochemistry of the diazosulfonate group is complex. Two mechanisms were found in the decomposition process: an ionic pathway in water (leading to diazonium salts and subsequent phenol groups)[36,37] and a radical process in less polar solvents (leading to biphenyl groups).[38] For thin films a radical process dominates which results in highly reactive intermediates and often in cross-linked products.[25] This

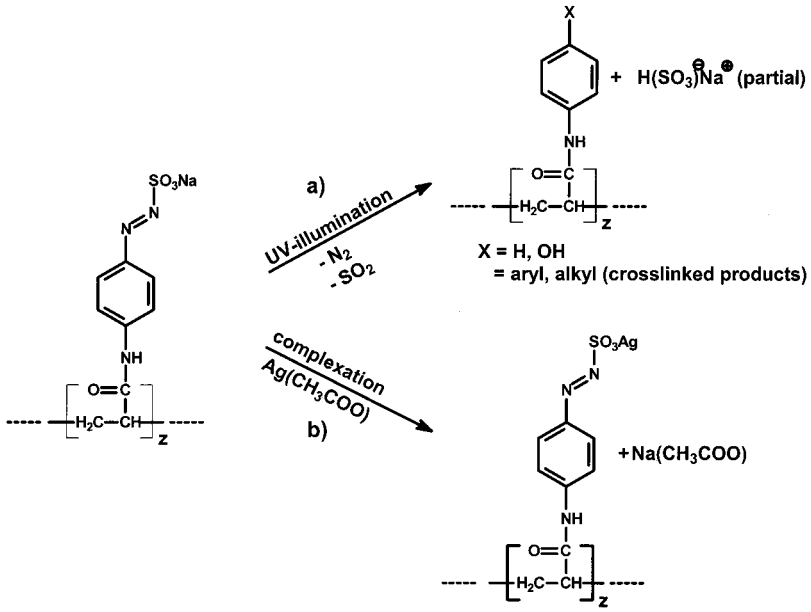

Figure 3. (a) Structural change of the sodium 4-acryloyl-aminophenyldiazosulfonate (APAS) unit with UV illumination and (b) after complexation with silver acetate. In (a) the polar diazosulfonate groups decompose under nitrogen evolution while in (b) the sodium ion is replaced by a silver ion.

change in the chemical structure of the diazosulfonate groups results in changes in solubility and surface polarity of the polymer films, both being suitable effects for novel applications of these polymers as photoresins.

For the purpose of selective metal complexation on ultrathin films of structured diazosulfonate polymers, the polymer structure had to be modified since an improved adhesion to the glass or silicon substrate is required. Furthermore, the polymer film has to stick to the substrate surface also without irradiation and under water or aqueous salt solution treatment. Thus, we designed a terpolymer structure containing 75 mol % MMA, 20 mol % of the photolabile diazosulfonate comonomer, and 5 mol % of an additional anchoring monomer (3-(trimethoxysilyl)propyl methacrylate). After certain variations in the polymer composition, we found that this composition seemed to be optimum, first to achieve a good film forming behavior with high mechanical strength of the film promoted by the MMA content of 75 mol %, second for relatively high content of photoactive groups (20 mol %) without losing the good polymer film properties, and third for having sufficient trimethoxysilyl groups (5 mol %) to allow permanent covalent bonding to the substrate but being able to prevent unwanted premature gelation.

Figure 1 depicts the terpolymer structure while Figure 3 exemplifies the possible changes in the polymer after UV irradiation. The diazosulfonate groups which provide sites for complexation can be removed by UV irradiation, but the general polymer structure including the anchoring group remains intact. Details on the polymer formation and the properties are reported elsewhere.[34]

This polymer was then used to prepare ultrathin films of 10−30 nm thickness via spin-coating onto glass or silicon wafers. The films were annealed to promote chemical bonding to the substrate via the anchoring groups. Nonattached polymer was removed by intense washing with water. The polymer films on silicon were characterized by atomic force microscopy (AFM) and ellipsometry to verify film thickness and surface smoothness (in the range of 1 nm rms). Polymer films prepared on glass were mainly used for UV exposure and complexation studies.

The transmission spectra of the untreated films depicted in Figure 2 show a clear absorption peak at $\lambda = 336$ nm, which is attributed to the $\pi-\pi^*$ transition of the diazosulfonate group.[25] The intensity of the absorption peak is consistent with the film thickness and can be used to calibrate film thicknesses. UV laser illumination cuts off the diazosulfonate group from the phenyl groups. The curves in Figure 2 show the decreasing intensity of the diazosulfonate absorption peak for an increasing number of UV laser pulses. This is a clear indication for complete decomposition of the diazosulfonate group.

To quantify successful decomposition of the diazosulfonate group, we applied a thorough XPS study. Following Figure 1, an untreated polymer film will show a significant contribution of Na^+-saturated $-SO_3^-$ units. After UV exposure the Na^+ peak in XPS should thus change drastically provided all $-SO_3^-$ is washed out and no unspecific Na^+ adsorption is present. A comparative analysis of the sodium content in our XPS data of untreated polymer films and illuminated ones reveals a sodium content clearly corresponding to the chemical composition of the terpolymer before and after illumination. After illumination and the first washing and sonicating in Millipore water, the sodium peak almost vanishes, and hence, the cracked sulfonate group was removed from the surface. This clearly proves chemical modification by UV laser exposure.

Once the UV-induced chemical modification of the thin terpolymer film was successful, we started to use as-prepared, but nonilluminated, films for the exchange of the sodium counterion of the diazosulfonate group by a silver ion using an aqueous silver salt solution. The structural change of the terpolymer upon metal salt complexation is described in Figure 3. As shown schematically, the sodium ion in the diazosulfonate group is replaced by the silver ion of the silver acetate. Again the attached metal ion may be used for XPS monitoring.

XPS data of the complexed polymer films clearly show a silver content of the sample surface. The UV absorp-

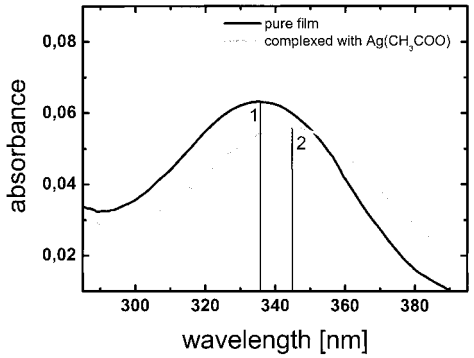

Figure 4. Absorption peak caused by the diazosulfonate group shifts by about 10 nm to higher wavelengths after chemical substitution of the sodium ion with silver.

tion of the diazosulfonate group depends first on the substitution pattern on the aromatic unit but to some extent also on the complexed metal salt.[25] So far, no UV absorption data for diazosulfonate silver salts have been reported. However, from early literature[32] the formation of stable low-molar-mass diazosulfonate silver salts is known which precipitated after addition of the silver salt solution to the dissolved sodium salt of a diazosulfonate derivative. Figure 4 shows transmission data of the absorption peak before and after metal salt complexation of the polymer film. A peak shift from 336 nm (1) to about 345 nm (2) indicates successful metal salt complexation of the terpolymer films since similar shifts are observed when sodium diazosulfonate polymers in solution are treated with silver salts.

After chemical reduction, the silver ions on the diazosulfonate groups are partially substituted again with sodium ions from the used $NaBH_4$ solution. Therefore, we expect a blue shift of the diazosulfonate peak back toward its original position at 336 nm. In fact, we do observe such a shift, although its amount measures only 3 nm.

So far, it was shown that we can prepare smooth and thin films of a new photolabile terpolymer on glass substrates. The photolabile diazosulfonate group was either destroyed with UV laser illumination and removed from the surface, or it was complexed with silver salt. The silver salt finally could be reduced to silver. All these chemical changes of the polymer film were observed via changes in the optical transmission spectra and quantitative XPS analysis.

At present, we were able to differentiate between illuminated and nonilluminated samples after being treated with exactly the same procedure for metal salt complexation and chemical reduction. However, the silver content does not differ as much as expected between surfaces of illuminated and nonilluminated films. Figure 5 shows the XPS spectra for two identically prepared samples after complexation and reduction. For the illuminated sample we expect no silver decoration and a theoretical ratio between carbon and nitrogen of C/N = 30 for the chemical composition of the surface. The measured ratio C/N = 34 is in good agreement with the expected value and proves that UV laser illumination and sonication successfully destroyed and removed almost all the diazosulfonate groups. Nevertheless, we observe residual silver ions on the surface (C/Ag = 206) so we conclude that silver also tends to bond nonspecifically to other sites in the polymer than the $-SO_3^-$ groups, e.g., phenolic groups which may result from the decomposition of the diazosulfonate group or, more likely, the ester and amide functions in the polymer backbone.

For the nonilluminated sample the ratio C/N is 14, which is close to the theoretical value of 10 and proves that the phenyldiazosulfonate unit was not destroyed. Nevertheless, there is not as much silver on the surface as expected (theoretically C/Ag = 30). For the nonilluminated sample the measured C/Ag ratio of 106 is a factor of 2 higher than for the illuminated surface, indicating additional adsorption achieved by the presence of diazosulfonate groups.

The factors on which the difference in silver content of the resulting surfaces depends most strongly are the duration of sonication in Millipore water after metal salt complexation and the film thickness.

For only short or no sonication, XPS analysis shows an excess of silver salt on the sample surface independent of whether the samples were illuminated or not. After chemical reduction this excessive silver salt forms silver clusters which we imaged by AFM and which gave rise to a typical absorption peak in the transmission data at $\lambda = 380-420$ nm, attributable to the plasmon resonance of small silver clusters.[33] So far, the best results were obtained with 10 min sonication on nonilluminated surfaces which leads to a small deficit of the silver content after complexation. The film thickness also influences the silver content of the sample surface.

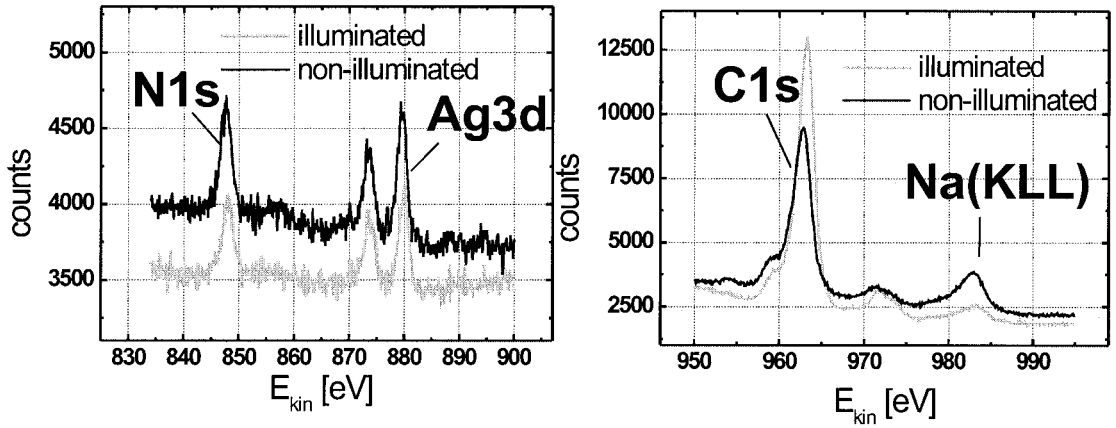

Figure 5. XPS spectra for two identically prepared samples after complexation and reduction. The relation between carbon and nitrogen is 14 and 34 for the illuminated and the nonilluminated sample, respectively. These values are in good agreement with calculations. The relation between silver and carbon shows a deficit for both samples with twice as much silver on nonilluminated areas.

Especially for very thin films (<10 nm) the results on illuminated and nonilluminated films do not differ much. All films studied had film thickness below 50 nm. In this range and the given UV absorption we can guarantee that the photoreaction was completed throughout the film, and no gradient should be formed in the chemical structure of the film upon irradiation. Nevertheless, the ratio surface area/bulk film changes with film thickness. The salt exchange reaction as well as the reduction of the silver salt should take place on the film surface as well as inside the bulk (or swollen) film phase. The unspecific binding of the metal salt can be considered mainly a surface reaction. In a somewhat thicker film metal salt complexation and reduction to elemental silver can take place inside the swollen polymer film whereas the unspecific binding will be favored on the surface. This can lead to some changes in the chemical composition of the film surfaces in very thin films (<10 nm) and films in the range of 20−40 nm.

The nonspecific binding of silver salt on the irradiated film might be due to interaction of the silver salt with polar amide groups in the polymer host structure. Furthermore, residual sulfonate groups that were not removed during washing, or decomposition products containing sulfone groups may add to an increased metal content as well.

Conclusions

In summary, this work presents a promising way for selective metallization of polymer thin films. The terpolymer used was synthesized from three monomers: the first responsible for spacing, the second for covalent bonding to the substrate, and the third providing functionality due to incorporation of a photolabile diazosulfonate group for metal salt complexation. Stable, smooth, and photolabile films were prepared by spin-coating onto glass substrates. The most striking results of these experiments on thin films are (i) the metal salt complexation of the diazosulfonate group and subsequent chemical reduction to metal clusters, (ii) the destruction of the photolabile diazosulfonate group by UV laser irradiation, and (iii) the difference of about a factor of 2 in metal content between the surfaces of UV illuminated and nonilluminated samples.

The results described above show the first step towards a successful selective metallization of diazosulfonate terpolymer thin films. Metal salt complexation and reduction of the nonilluminated films was proven. Although the resulting films do not yet show metallic surface layers, a significant change of the surface chemical composition was obtained, especially between illuminated and nonilluminated films. Careful optimization of the complexation and reduction processes should lead to a more selective metallization.

Such films therefore are promising candidates for optical structuring of polymers in order to create nanosized metallic structures of arbitrary desired shape.

Acknowledgment. We gratefully acknowledge the financial support from the Bundesministerium für Bildung und Forschung (Ch. Loppacher, Förderkennzeichen: 03N8610), Industrieförderung (S. Trogisch), SMWK (A. Zherebov), and the DFG (Forschergruppe 335).

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MA0114335