

Metalization of Polymer Beads via Polymer-Supported Hydrazines as Reducing Agents

NIYAZI BICAK,¹ ŞANA SUNGUR,² NÜKHET TAN,² FARID BENSEBAA,³ YVES DESLANDES,³

¹Istanbul Technical University, Chemistry Department, Maslak, 80626 Istanbul, Turkey

²Kadir Has University, Faculty of Engineering, Selimpaşa, Istanbul, Turkey

³Institute for Chemical Process and Environmental Technology, National Research Council of Canada, 1200 Montreal Road, Ottawa, Ontario, K1A 0R6, Canada

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ABSTRACT: A new method for depositing metal onto a polymer surface has been developed in which the metal coating of polymer beads is performed with hydrazine functions as reducing agents on the surface of the polymer itself. In this study, glycidyl methacrylate–methyl methacrylate–divinyl benzene terpolymer was prepared as spherical beads with a suspension polymerization methodology. Beads of the polymer sample (210–420- μm fraction) containing 3.4 mmol g⁻¹ epoxy were treated with an excess of hydrazinium hydroxide to yield a polymer with 2.3 mmol g⁻¹ hydrazine functions. The hydrazine functions on the polymer surfaces were efficient in metal reductions. Therefore, the modified bead polymer samples, when soaked in aqueous ammonia solutions of Ni(II), Ag(I), and Cu(II) ions (0.1 M), were covered rapidly by the corresponding zero-valent metal ions. Metal deposition took place almost quantitatively (ca. 4.5 mmol/g of the polymer) within 60 min of the contact times. The accumulations of metal were followed visually and occurred only on the polymer beads. There was no evidence that the reaction occurred within the solution. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 748–754, 2002; DOI 10.1002/pola.10158

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INTRODUCTION

The deposition of zero-valent metals onto polymer surfaces has received much attention for its potential applications in preparing light-weight mirrors,¹ solar energy converters,² and catalysts.³ Even though the polymer-assisted microdispersion of metal sols was performed half a century ago,⁴ the metalization of polymer surfaces is a relatively new area of research. Indeed, chemical vapor deposition has been actively studied since

its emergence in 1982.⁵ In this method, thin metal films are produced by thermal decomposition of some metal compounds under high vacuum. The metal coating of polymer surfaces by direct deposition from metal-ion solutions has been termed *electroless plating*. In the earliest method of metal plating, a polymeric surface is first activated with a strong reducing agent such as SnCl₂ or CuCl and is then treated with the appropriate metal-ion solution.⁶ In more recent methods, metal ions in aqueous solutions are seized by ligating groups such as amino, carboxyl, or quaternary amino groups on polymer surfaces. Thereafter, these ions are reduced by a suitable reducing agent such as sodium hypophosphite or dimethylamino

Correspondence to: N. Bicak (E-mail: bicak@itu.edu.tr)

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borane. Details of the preparation for the electroless plating of vinyl benzyl ammonium-based polymer beads were given by Warshawsky and Upson.⁷ In those methods, the deposited metals are mostly amorphous and nonuniform and so lack metallic luster. With this approach, metal-plated polymer particles that are up to 10% noble metal have been obtained.

Multimetallized layers on polymer surfaces have also been achieved with subtractive and additive deposition techniques. In the subtractive deposition technique, metal-coated polymers are immersed in a different metal-ion solution, and metals on the surfaces are replaced with another metal with less negative reduction potential. In the additive method, additional metal deposition occurs on premetallized surface by the catalytic effect of existing metal used together with a reducing agent. All the methods involve the use of external reducing agents for the metalization of polymer surfaces. Recently, highly reflective silver-coated polyimides were prepared by the heating of silver salts of polyamic acids at elevated temperatures.⁸ To the best of our knowledge, no reports have been published so far on the use of polymer-bound reducing agents for the deposition of zero-valent metals on the same polymer.

In this study, we describe the metalization of glycidyl methacrylate (GMA)-based crosslinked polymer beads with hydrazine functions. The role of the hydrazine functions in the mechanism of metal deposition from ammoniacal solutions of Ni(II), Cu(II), and Ag(I) was investigated.

EXPERIMENTAL

All the chemicals used—GMA (Fluka), methyl methacrylate (MMA; Fluka), divinyl benzene (DVB; Aldrich), and hydrazinium hydroxide (100%; E. Merck)—were analytical-grade chemicals and were used without any further purification.

Preparation of GMA–MMA–DVB Terpolymer Beads

The beads were prepared by the suspension polymerization of a 120-mL toluene mixture of GMA (0.4 mol), MMA (0.5 mol), and DVB (0.1 mol) with 350 mL of water as the continuous phase. Details of the procedure are given elsewhere.⁹ Polymer beads were sieved, and 210–420- μm fractions were used in the subsequent reactions.

The epoxide content of the fractions was determined to be 3.4 mmol g^{-1} by the pyridine–HCl method.¹⁰

Modification of the Polymer Beads with Hydrazine

Fourteen grams of the polymer beads was mixed with 30 mL of hydrazinium hydroxide (100%) in a 250-mL flask equipped with a reflux condenser and a mechanical stirrer. While stirring, the mixture was refluxed for 1.5 h. After cooling, it was filtered and washed with an excess of distilled water that had been deaerated with a flow of nitrogen gas. The product was dried at 50 °C for 24 h *in vacuo*. The yield was 16.2 g.

The surface area of the polymer beads, as measured by the Brunauer–Emmett–Teller method, was 0.384 $\text{m}^2 \text{g}^{-1}$.

Determination of the Hydrazine Content

The hydrazine content of the polymer was determined with a modified periodate method¹¹ as follows: 0.5 g of the polymer sample was mixed with 10 mL of CCl_4 and 5 mL of 0.1 M periodic acid in a tightly closed bottle and was covered with aluminum foil. The mixture was stirred with a magnetic stirrer for 48 h, and 5 mL of the organic phase was separated quickly with a separator funnel. The iodine content of the organic phase was assayed by the thiosulfate titration method described in the original procedure. This measurement indicated a hydrazine content of 2.3 mmol g^{-1} .

Metal Deposition onto Polymer Particles

Deposition of Nickel

The polymer sample (0.5 g) was introduced into a mixture of 25 mL of a 0.1 M NiCl_2 solution and 5 mL of a concentrated NH_3 solution (25%) in a closed bottle. During swirling, the immediate precipitation of the metal onto the particles was easily followed visually. However, no metal particles were observed in the solution phase. The mixture was shaken with a continuous shaker for 24 h at room temperature. The mixture was filtered and washed with deaerated water. The filtrate and washings were combined and diluted to 250 mL with water. Metallized beads were dried *in vacuo* at 50 °C for 24 h. The yield was 0.62 g. The sample was stored in a tightly closed bottle.

Table 1. Metallization Characteristics of the Resin

Metal Ion	Reaction Temperature	Weight Increase % ^a	Deposited Metal (mmol g ⁻¹) ^b	Metal Depletion in Solution (mmol g ⁻¹) ^c	M(0)/H (mol/mol) ^d	Metallization Yield (%) ^e
Ni (II)	Room temperature	25.0	4.50	4.39	1.95	97.5
Cu (II)	60 °C	27.5	4.32	4.51	1.88	94.0
Ag (I)	Room temperature	47.8	4.55	4.62	1.98	99.0

^a By metal deposition.^b By analysis of acid-leaching solution.^c By analysis of unreacted metal contents of the solutions.^d Reduced metal per mole of hydrazine.^e Yields based on 2 mmol metal per mole of hydrazine function.

Deposition of Copper

The same procedure was applied with a CuCl₂ · 6H₂O solution (25 mL, 0.1 M) with the difference that the metallization was accomplished at a constant temperature of 60 °C provided by a thermostated oil bath. Stirring of the solution was performed with a continuous shaker to avoid cracking of the bead particles with a magnetic stirrer. With the same procedure being followed, 0.64 g of a copper-plated sample was obtained.

Silver Deposition

To 25 mL of a 0.1 M AgNO₃ solution, 2.5 mL of a 1 M KOH solution and 5 mL of a concentrated NH₃ solution were added successively. After stirring for 10 min, the solution was filtered. Hydrazine resin (0.5 g) was added to 50 mL of the solution, and the mixture was shaken for 48 h at room temperature. Silver bead particles were filtered and recovered by a similar procedure described previously. The yield was 0.74 g.

Analysis of the Precipitated Metal Contents

The metal contents within the metallized polymer beads were determined by analysis of the final metal-ion solutions (method A) and by analysis of acid-leaching solutions of the bead samples (method B).

Method A

In this method, metal contents of residual liquors were analyzed. For this purpose, the solutions that were in contact with the polymer beads were filtered and diluted to 250 mL. Aliquots of 10 mL of each solution were used to assay the metal

concentrations. Ni(II) was determined by an ethylenediaminetetraacetic acid titration method.¹² Cu(II) was determined by an iodometric method.¹³ Ag(I) was determined by the Volhard method.¹⁴ From the differences of the final and initial concentrations, the quantities of the accumulated metals were calculated.

Method B

Metal-coated polymer particles (0.5 g) were mixed with 20 mL of 2 M HNO₃ solutions. The mixtures were stirred for 1 h at room temperature, filtered, and washed with distilled water. The filtrate and washings were combined and then diluted to 100 mL. Metal contents of the solutions were determined with the same analytical procedures described previously. The data are tabulated in Table 1.

X-Ray Photoelectron Spectroscopy (XPS)

For XPS, the powders were deposited onto a stub without further treatment. They were analyzed with an Axis HS X-ray photoelectron spectrometer (Kratos, Manchester, United Kingdom). The analyzed area was about 1 mm². Monochromatized Al K α radiation was used for excitation, and a 180° hemispherical analyzer with a three-channel detector was employed. The X-ray gun was operated at 15 kV and 20 mA. The spectrophotometer was operated in the fixed analyzer transmission mode throughout the study with electrostatic magnification. Survey and high-resolution spectra were collected with 160- and 20-eV pass energies, respectively. The pressure in the analyzer chamber was 10⁻⁸ to 10⁻⁹ Torr. An electron flood gun was used to neutralize the charge dur-

ing the experiment. Binding energies were referenced to the carbon-carbon bond, which was assigned a binding energy of 285 eV. The atomic compositions were estimated with standard software provided with the instrument and with the following sensitivity factors: 0.25 for C1s, 0.66 for O1s, 0.42 for N1s, and 1.00 for F1s.

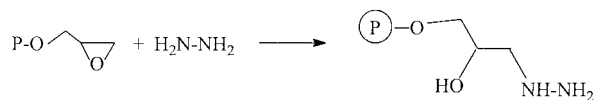
Scanning Electron Microscopy (SEM)

SEM micrographs were taken as follows: A small amount of each sample was placed in a beaker with isopropanol and shaken in an ultrasonic bath for 10 min. A few milligrams of the mixture was transferred to a glass slide cover and allowed to dry. The slide cover was then sputter-coated with gold. The analysis was performed with a JEOL JMS 5300 scanning microscope. Particle size was determined by the comparison of particles in the photographs to the clear bar at the right hand corner of the photographs.

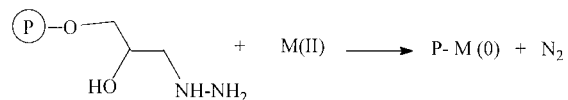
RESULTS AND DISCUSSION

Here we describe the use of polymer-supported reducing agents for metal deposition onto polymers. A GMA-based polymer was chosen as the support because of its easy functionalization through the epoxide functions involved. It was prepared by the terpolymerization of GMA (0.4 mol), MMA (0.5 mol), and DVB (0.1 mol) mixtures by suspension polymerization methodology with a maleic acid-styrene copolymer as the suspension stabilizer. The epoxy group involved was a suitable reactive group for modification under mild conditions.

Those beads with a diameter between 210 and 420 μm were used for further reactions. The hydrazine used as a reducing agent was incorporated simply by the reaction of the terpolymer beads with an excess of hydrazinium hydroxide (100%; see Scheme 1). The hydrazine content of the resulting polymer (2.3 mmol g^{-1}) implied 77.1% conversion yields of the epoxy functions. Apparently, the remaining portion of the epoxy groups might have been consumed by water in the



Scheme 1



Scheme 2

hydrazine to give vic-diol functions at the same time.

Metalization of the Beads

The metalization of the polymer beads was achieved by a reaction with ammoniacal Ni(II)-, Cu(II)-, and Ag(I)-ion solutions. The process was so rapid that when the Ni(II)-ion solution was added dropwise to a stirred aqueous mixture of 0.5-g bead particles, the color of the hexamine complex disappeared less than 30 s after the addition of each drop. The aqueous solution became clear after completion of the reduction. This indicated that no metal precipitation occurred in the solution. The metal reduction process can be represented as shown in Scheme 2.

In the case of silver, an aqueous solution became light brown at the beginning of the interaction and thereafter turned into a colorless solution. The silver particles gained a typical metal color when dilute AgNO_3 solutions were used, presumably because of the slow accumulation of Ag(0) crystals onto the surfaces as stated in the literature dealing with the reduction of silver with hydrazine. Deposition from concentrated solutions (0.1 M) gave gray silver coatings. Most likely, highly reflective silver plating may be achieved by slow deposition from dilute solutions (5.10^{-3} M). The optimization of the preparation method with respect to the reflectivity of the beads needs further investigation and does not fall within the scope of this article.

Unlike silver deposition, copper deposition takes place at elevated temperatures, typically greater than 50 $^\circ\text{C}$. We found that at 60 $^\circ\text{C}$, the deposition of copper onto the polymer beads took place with reasonable rates. In Table 1, the amounts of the deposited metals in the batch operation have been listed.

Although the metal deposition process is heterogeneous in nature, it proceeded rapidly under the conditions studied. As expected, the kinetics of metal precipitation have a close relationship with the stirring rates. To acquire relevant information about the order of the deposition rates, we followed the reactions kinetically by analyzing

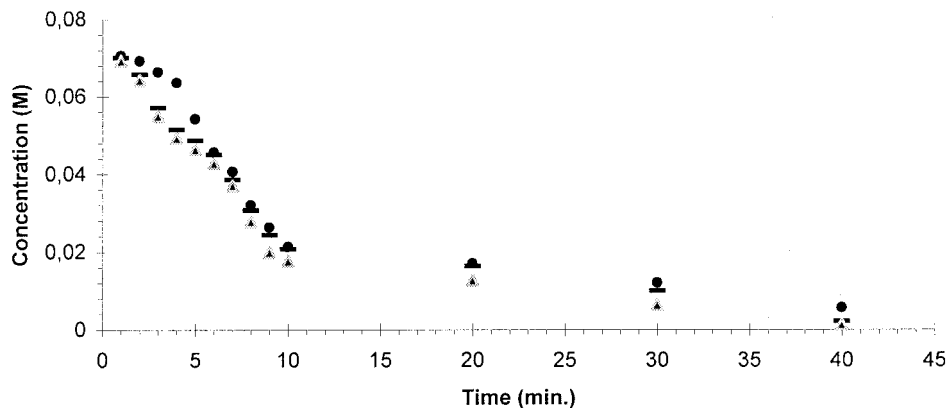


Figure 1. Concentration versus time for the metal depositions (35 mL of 0.0714 M metal-ion solutions [(▲) Ni(II), (—) Cu(II), and (●) Ag(I)] in contact with 0.5-g polymer samples).

aliquots taken at appropriate time intervals. Figure 1 clearly shows that reactions took place within 60 min for Ni(II) (0.1 M) and Cu(II) (0.071 M) starting solutions. Because the oxidation product of hydrazine is nitrogen in metal-ion reduction reactions, the total reaction is expected to proceed as shown in Scheme 3.

According to this reaction, 1 mol of hydrazine function is expected to generate 2 mol of elemental copper and nickel from their divalent salts. Based on the hydrazine content of the polymer, the theoretical metal reducing capacity should be 4.6 mmol/g of polymer. As seen in Table 1, in each case the amounts of accumulated metals are very close to the 4.6 mmol g⁻¹ limiting values. The data obtained by the analysis of the metal contents of the metalized beads approximately match the values obtained from the differences of the initial and final metal-ion contents of the aqueous solutions. For nickel and copper deposition, these values are consistent with the aforementioned redox reaction. Practically, 1.88–1.95 mol of Cu(II) and Ni(II) is reduced per mole of hydrazine function, which is almost equal to the theoretical value. In other words, the reactions proceed almost quantitatively, and about 2 mol of Ni(0) and Cu(0) is deposited for each mole of the hydrazine function. For silver, the situation seems to be different. If the same reaction took place with monovalent silver, there would be 4 mol of silver metal formed per mole of hydrazine. However,

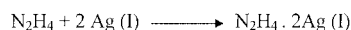
according to earlier reports,¹⁵ the reaction of hydrazine itself with silver salts proceeds through the formation of an addition product (Scheme 4).

The reaction is followed by spontaneous decomposition of the adduct to give metallic silver. Therefore, this reaction justifies the formation of 2 mol of elemental silver by 1 mol of hydrazine function on the polymer. However, the data on metal precipitation reveal that almost all of the hydrazine functions are being utilized in the metal reductions, although the reactions with the beads are heterogeneous in nature. There exist no hydrazine functions remaining that would be inaccessible on the bead particles because they have been incorporated by posttreatment of the crosslinked prepolymer. This implies that the final quantity of deposited metals is proportional to the hydrazine contents, and one can collect predetermined quantities of zero-valent metals by loading any desired amount of hydrazine function onto the polymer.

Moreover, marked increases in the polymer masses can be regarded as more direct evidence for the metalization (Table 1). If we assume increasing masses are only due to metal depositions, a 47.8% mass increase for silver will correspond to 4.43 mmol g⁻¹ silver, which is close to the value (4.62 mmol g⁻¹) obtained by the analytical method. By a similar analogy, 4.31 and 4.33 mmol g⁻¹ deposits of nickel and copper are comparable to those predicted by the analytical procedures.



Scheme 3



Scheme 4

Table 2. Binding Energy and Relative Concentration of the Various Metal Species Found in the XPS Analysis

Metal	Binding Energy (eV)	Relative Atomic Concentration ^a (%)	Assignments and Binding Energy (eV) ¹⁶
Cu2p	932.9	0.83	Cu metal: Cu2p _{3/2} = 932.7 CuO: Cu2p _{3/2} = 933.7 CuOH: Cu2p _{3/2} = 934.7
	935.1	0.39	
	940.2	0.25	
	943.9	0.29	
Ag3d	944.0	0.25	AgO: 367.2 Ag metal: 368.5
	368.6	25.77	
Ni2p	856.2	0.78	Ni metal: Ni2p _{3/2} = 852.5 NiO _x : Ni2p _{3/2} = 856.0
	859.8	0.42	
	862.8	0.40	

^a Atomic concentrations were given based on C, O, N and metal elements. Because hydrogen is not detected with XPS, it is not included in the total elemental analysis.

Metalized polymers have been analyzed with XPS. Data for Cu-, Ni-, and Ag-coated beads are summarized in Table 2. In this table, we report only the XPS data from the orbital 2p for Cu, 3d for Ag, and 2p for Ni. For the Cu sample, the peak at 932.9 eV is assigned to metallic copper. The other Cu peaks are assigned to oxidized copper. For silver, only one peak has been detected. On the basis of the reported literature value of the oxidized and metallic Ag, we conclude that the Ag is in the metallic state. For Ni, we have not been able to detect any trace of the metallic state. This could be assigned to the rapid transformation from the metallic state to the oxidized state. We tried to reduce the aging time between the preparation and the XPS analysis to a minimum (ca. 1 h). However, this experience has also resulted in Ni-coated beads without any trace of zero-valent nickel.

SEM pictures of the metalized beads show nice spherical particles with a homogeneous appearance. An SEM picture of copper-deposited beads is given as an example in Figure 2. A relatively regular copper surface is observed on a few 100- μm bead particles.

The fact that no zero-valent nickel was observed might be due to the high susceptibility of the fresh nickel surfaces to air oxygen. This assumption was confirmed qualitatively with a separate experiment as follows: The resin sample (0.3 g) was nickelized by the same procedure. After repeated washings with deaerated water, without drying, the beads were reacted with 10 mL of an ammoniacal Cu(II) solution (0.1 M). The accumulation of copper metal on the bead surface

in few minutes confirmed the presence of the zero-valent nickel on the bead surfaces. Only zero-valent nickel (having less reduction potential) is able to reduce Cu(II) from its solution according to the common redox reaction (Scheme 5).

As a result, it can be deduced that the nickel is also deposited in its elemental form but undergoes rapid oxidation by air oxygen during handling. The high surface area (0.384 m² g⁻¹) might be responsible for its quick oxidation. Surface passivation or storage in reductive solutions would be useful for protecting the nickelized beads for further use (e.g., hydrogenation catalysts) In this study, we did not attempt to stabilize the nickel in its elemental form. This will be the subject of another study.

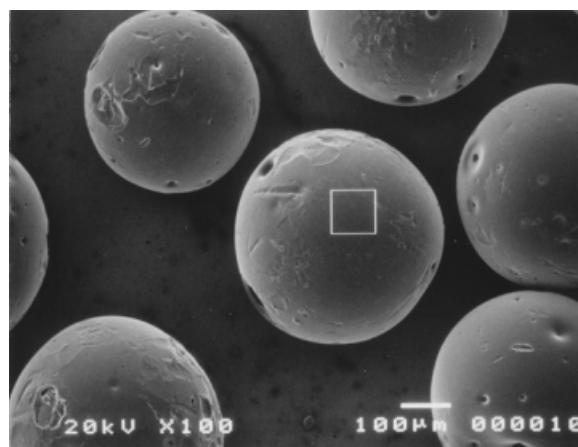
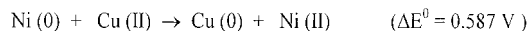


Figure 2. SEM micrograph of the copper-deposited polymer beads (original magnification, 8000 \times ; the conditions are reported in the Experimental section).

**Scheme 5****CONCLUSIONS**

The use of polymer-supported hydrazine as a reducing agent is a very useful approach for the direct deposition of Ni(0), Cu(0), and Ag(0) from aqueous solutions. All metal precipitation seems to occur at the surface of the polymer beads. This is an advantage of the proposed method over the other methods that use external reducing agents. The method presented seems to be beneficial and can be extended to the preparation of metalized polymer films for electronic circuits and so forth.

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