# In-situ Generation of Gold, Platinum and Palladium Nanoparticles in N-isopropylacrylamide-surfmer Copolymer Hydrogels and Catalytic Activity of the Gels

Katharina Kraus, Tamara Mielke, Tatjana Friedrich, and Bernd Tieke

**Abstract**

Preparation and catalytic activity of N-isopropylacrylamide (NIPAM)/surfmer copolymer hydrogels containing gold, palladium and platinum nanoparticles are described. The functional hydrogels were obtained in three steps. First a thermoresponsive copolymer gel was prepared upon $^{60}$Co-gamma irradiation of a micellar aqueous solution of NIPAM and (2-methacryloyloxyethyl)dodecyldimethylammonium bromide (MEDDAB) or (11-methacryloyloxyundecyl)trimethylammonium bromide (AUTMAB). Secondly tetrachlorometalate anions were introduced in the gel upon ion exchange of the bromide counterions of the positively charged surfmer head groups. For this purpose, the gel was de-swollen at 50 °C and re-swollen in aqueous solution of tetrachloroauric acid, sodium tetrachloropalladate, or sodium tetrachloroplatinate at 20 °C. Thirdly, the metal nanoparticles were in-situ generated by exposing the de-swollen gel to an aqueous solution of sodium borohydride, which led to re-swelling and reduction of the complex anions. The formation of nanoparticles caused an immediate colour change of the gel from yellow or brown to golden black or black. TEM studies indicate aggregates of nanoparticles of approximately 3.5–5.3 nm in diameter. The metal-containing gels catalyze the reduction of 4-nitrophenolate (4-NP) into 4-aminophenolate below the lower critical solution temperature (LCST) and at high osmotic pressure, where the gels are highly swollen. NIPAM/MEDDAB gels are active at 20 °C and 30 °C, whereas at 40 °C (readily above the LCST of 29 °C) the activity is low and comparable with the metal-free gel. NIPAM/AUTMAB gels with large counterion dissociation are still active at 40 °C although the LCST is only 33.8 °C. Further studies indicate that the gold-containing gels exhibit the highest catalytic activity, and that the gels can be repeatedly used for catalysis because the metal nanoparticles are only slowly washed out.

**Keywords**

Hydrogel • Gold • Palladium • Platinum • Nanoparticle • Catalytic activity • N-isopropylacrylamide • Surfactant monomer

## Introduction

In recent years intelligent hydrogels have been subject to numerous research studies [1] because of their reversible volume phase transitions [2] in response to external stimuli such as temperature [3], pH [4], magnetic field [5], light [6], solvent compositions [7] and ionic strength [8]. Most of the research activities were concerned with hydrogels based on cross-linked poly-N-isopropylacrylamide (pNIPAM), which exhibit a reversible volume transition from a clear, swollen, hydrophilic state to a turbid, shrunken, hydrophobic state, if heated to temperatures higher than 32 °C [9]. As recently demonstrated, the poor mechanical stability of

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K. Kraus • T. Mielke • T. Friedrich • B. Tieke (✉)
Department of Chemistry, University of Cologne, D-50939 Cologne, Germany
e-mail: tieke@uni-koeln.de

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pure pNIPAM hydrogels can be considerably improved if copolymer hydrogels of NIPAM and surfactant monomers (surfmers) are prepared [10–13]. The copolymer gels can be obtained in a single-step reaction by exposing a micellar aqueous comonomer solution to gamma irradiation.

The use of cationic surfmers (surfactant monomers, polymerizable surfactants) as comonomer results in the formation of positively charged gels. As recently shown, the halide counterions can be easily exchanged for other anions [14–17]. By means of the ion exchange, functional hydrogels with interesting photophysical [14] and photochemical properties [15] could be prepared. Inorganic nanoparticles could be generated in-situ such as Prussian Blue particles [16] or catalytically active palladium nanoparticles [16]. Especially the in-situ generation of metallic nanoparticles is of interest, because a new type of catalytic gel with versatile and repeated use may become accessible. In a previous publication [16] we briefly communicated the catalytic activity of Pd-containing NIPAM-MUTMAB copolymer gels prepared upon radical copolymerization of NIPAM and MUTMAB (11-methacryloyloxyundecyl)trimethylammonium bromide in micellar solution. In our present article, a comprehensive study on the in-situ preparation of gold, platinum and palladium nanoparticles in NIPAM-surfmer copolymer gels and their use as catalysts in hydrogenation reactions is presented. Different from the previous communication, the gels were prepared upon radiation-induced copolymerisation of NIPAM and (2-methacryloyloxyethyl) dodecyldimethylammonium bromide [18, 19] (MEDDAB) or (11-acryloyloxyundecyl)trimethylammonium bromide (AUTMAB) [20] in an aqueous micellar solution. The two surfmers were chosen because of their different structure with the reactive unit either at the tail or head of the molecule (T- or H-type surfmer), which is accompanied by either a strong or weak counterion dissociation [20] leading to hydrogels with either strong or weak osmotic pressure and swelling behaviour. Use of gamma irradiation is advantageous because it homogeneously penetrates the sample and no additives such as initiator, accelerator, or cross-linker are needed. After in-situ preparation of the particles, the gels were studied on their catalytic activity in the reduction of 4-nitrophenol (4-NP) to yield 4-aminophenol. Spectroscopic and microscopic measurements were used in order to characterize the gel structure and morphology, and their catalytic activity.

## Experimental Part

### Materials

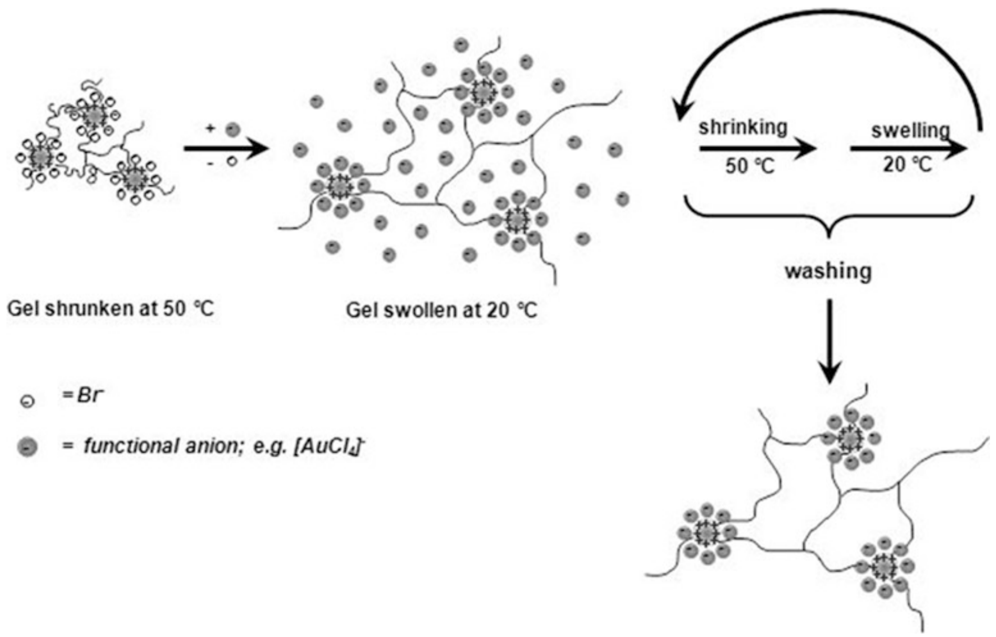
(2-Methacryloyloxyethyl)dodecyldimethylammonium bromide (MEDDAB) and (11-acryloyloxyundecyl)trimethylammonium bromide (AUTMAB) were synthesized according to the literature [18–20]. N-Isopropylacrylamide (NIPAM) was recrystallized from toluene and n-hexane (volume ratio: 1:2). MilliQ water was used for all experiments. Sodium tetrachloropalladate, sodium tetrachloroplatinate, and tetrachloroauric acid were purchased from Acros and used without further purification. MilliQ water was used for all experiments.

**Preparation of hydrogels**. Hydrogel samples were prepared in screw-capped glass tubes at 20 °C. Monomer solutions containing 10 wt% NIPAM and 1 wt% MEDDAB in degassed MilliQ water were homogenized using a Vortex mixer, aged for 24 h and copolymerized in a one-step reaction. The gels were copolymerized using $^{60}$Co-gamma-irradiation, the dose rate being 300 Gy/h, and the total radiation dose being 80 kGy. The irradiation was carried out at Beta Gamma Service in Wiehl, Germany.

**Exchange of counterions**. The exchange of bromide counterions for inorganic complex ions was accomplished by using the thermosensitive swelling and shrinking of the gels as described in Scheme 1 [14–16]. First the gels were heated to 50 °C for 8 h to cause shrinking. Then they were re-swollen in an aqueous solution containing the inorganic complex anions at 20 °C for time periods between 1 and 21 days. The concentration of the aqueous solutions containing $Na_2PdCl_4$, $HAuCl_4$ or $Na_2PtCl_4$ was always 1 mM. The shrinking/re-swelling cycle was followed by two further shrinking/re-swelling cycles in pure MilliQ water in order to wash out all anions which were not fixed to the gel matrix.

**In situ generation of $Au^0$, $Pd^0$, and $Pt^0$ nanoparticles**. Hydrogels containing $AuCl_4^-$, $PdCl_4^{2-}$, and $PtCl_4^{2-}$ were shrunken at 50 °C for 8 h and re-swollen in an aqueous $NaBH_4$ solution at 20 °C for 24 h, the sodium borohydride concentration being 13 mM. The shrinking/re-swelling cycle was followed by two further shrinking/re-swelling cycles in pure MilliQ water in order to remove excess sodium borohydride or reaction products from the reduction of the inorganic complex anions.

**Reduction of 4-nitrophenol with sodium borohydride**. The reduction of 4-nitrophenol was carried out in an aqueous solution of 4-nitrophenol, the concentration being 0.05 mmol/L. The catalytic activity was studied at 20 °C and 30 °C, i.e., below the volume phase transition temperature of the gel, and at 40 °C, i.e., above the transition temperature. Prior to the experiments, the copolymer gels containing the nanoparticles were re-swollen to their original size in MilliQ water. Then the gel was put in the aqueous 4-nitrophenol solution and 5 mmol/L sodium borohydride were added. In order to study the catalytic reduction quantitatively, every 10 min a sample was taken from the 4-nitrophenol solution and a UV-spectrum was recorded. For comparison, the reaction was also studied without addition of the catalytic gel.



**Scheme 1** Model of electrostatic self-assembly of functional anions

## Methods

UV/Vis absorption spectra were recorded using a Perkin Elmer Lambda 14 spectrometer. The spectra were corrected by subtracting the background signal. Energy dispersive X-ray (EDX) spectroscopy was performed using a Zeiss Neon 40 scanning electron microscope (SEM) equipped with an Inca Dry Cool EDX detector for microanalysis. The gels were dried in an oven at 50 °C, fixed to the microscope holder using conductive silver paste, and coated with carbon (EMITECH K950X). The software Inca was used for the EDX measurements, and the experimental error was about 5 % of the measured value. TEM measurements were carried out using a LEO EM 912 Omega electron microscope.

For the study of the swelling/de-swelling behaviour the hydrogels were immersed in 150 ml Milli-Q-water (at 20 °C or 50 °C) for different time periods. The water uptake (or release) was determined gravimetrically by weighing the hydrogel prior and subsequent to the water treatment. The degree of swelling $S$ was calculated as

$$S = \frac{W_t - W_0}{W_0}, \tag{1}$$

where $W_t$ and $W_0$ are the weights of the sample subsequent and prior to swelling in water. $S$ was determined as a function of time at constant temperature.

## Results and Discussion

### Preparation of the Hydrogels

Let us first describe the preparation and functionalization of the gels. The copolymer hydrogels were prepared from a micellar aqueous solution of NIPAM and one of the two surfactant comonomers (2-methacryloxyethyl)dodecyldimethyl ammonium bromide (MEDDAB) or (11-acryloyloxy-undecyl)trimethylammonium bromide (AUTMAB) using $\gamma$-irradiation. The radiation dose was always 80 kGy, the dose rate was ca. 300 Gy/h. The low dose rate was chosen after it was found that dose rates higher than 1 kGy/h lead to brittle gels with high cross-linking density, recognizable by the formation of voids and crazes in the samples. At dose rates lower than 500 Gy/h homogeneous and defect-free gels were obtained. Due to the copolymerization with the cationic surfmer, the resulting hydrogels were positively charged. The hydrogels were always prepared from comonomer solutions containing 10 wt% NIPAM and 1 wt% surfmer.

### In-situ Generation of Metal Nanoparticles

After preparation the NIPAM/MEDDAB gels were used for in-situ generation of gold, palladium, and platinum nanoparticles, whereas the NIPAM/AUTMAB gels were only used for generation of palladium particles. Let us first describe

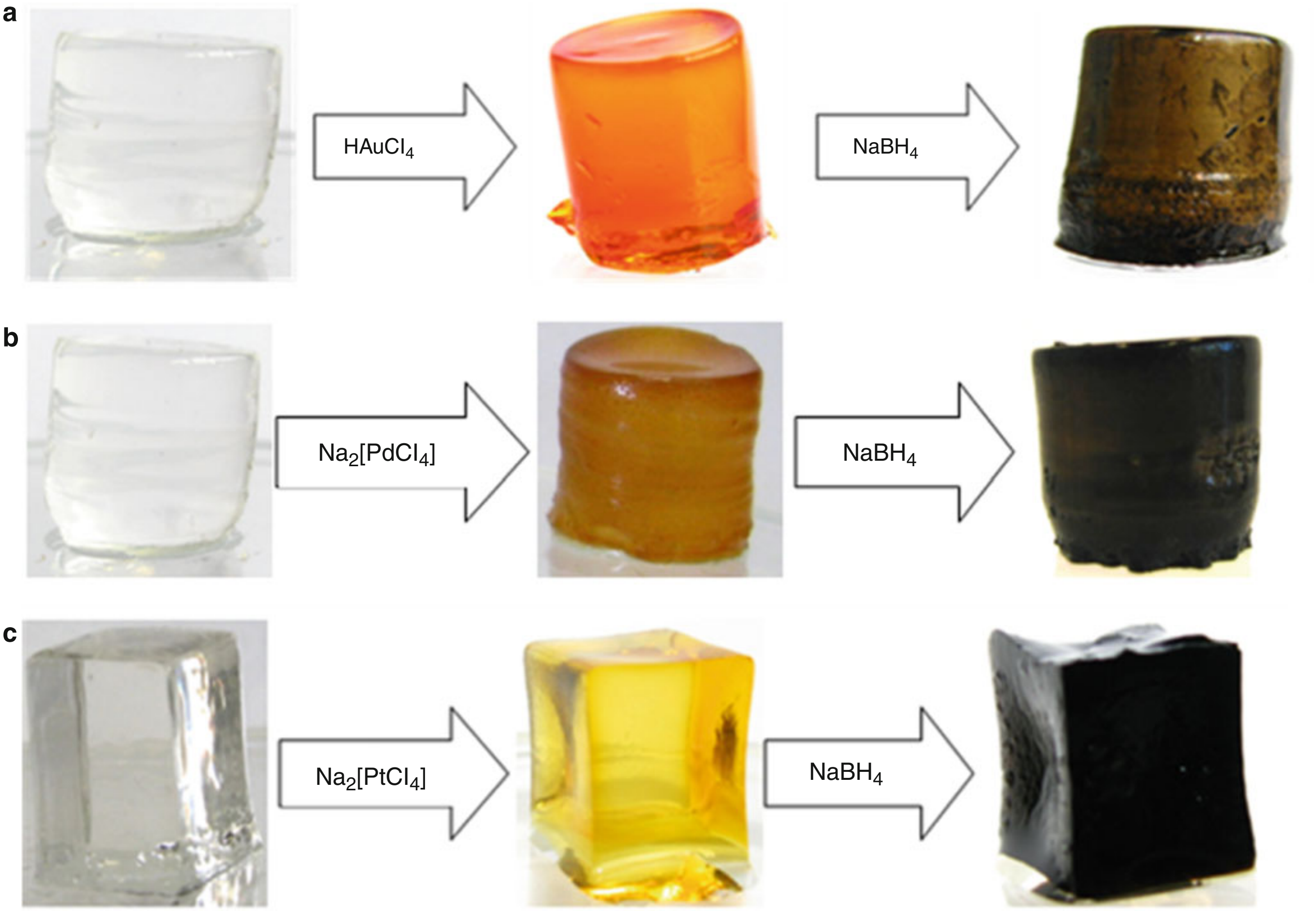


**Fig. 1** Photographic images of NIPAM/MEDDAB copolymer hydrogel before (**a–c**, *left*) and after electrostatic adsorption of tetrachlorometalate anions (*middle*), the anions being tetrachloroaurate (**a**), tetrachloropalladate (**b**), and tetrachloro-platinate (**c**), and after reduction with $NaBH_4$ to yield gold (**a**), palladium (**b**), and platinum nanoparticles (**c**) in the gel (*right*)

the generation of gold particles in NIPAM/MEDDAB gels. A method recently applied for preparation of gold nanoparticles in polyelectrolyte hydrogels was adapted [21]. First the freshly prepared gels were de-swollen at 50 °C for 8 h. Then the gels were immersed and re-swollen in an aqueous solution of tetrachloroauric acid. The hydrogel samples changed their color from originally colorless to red orange indicating the ion exchange (Fig. 1). It took several days until the exchange process was complete. After approximately a week the gels were repeatedly shrunken and re-swollen in pure water in order to remove excess tetrachloroaurate ions, which were not electrostatically bound to the gel matrix (see also Scheme 1). For preparation of the nanoparticles, the gels were first de-swollen at 50 °C, and then swollen in an aqueous solution containing sodium borohydride. The borohydride anions reduced the $AuCl_4^-$ anions to form $Au^0$ nanoparticles. This process was accompanied by a color change of the gel from red orange to black-golden (Fig. 1a). The distribution of the nanoparticles in the gels was strongly a function of the exposure time to the tetrachloroaurate solution. Cross-sections of gels immersed in the solution for only 24 h indicate a very inhomogeneous distribution of the gold particles after the reduction step, the center of the gel being nearly colorless without any particles present (Fig. 2). However, if the gel was immersed for 3 weeks, the distribution of the particles was homogeneous.

For generation of $Pd^0$ and $Pt^0$ nanoparticles the NIPAM/MEDDAB gels were swollen in aqueous sodium tetrachloropalladate or sodium tetrachloroplatinate solutions, and subsequently reduced with sodium borohydride. The method was analogous to the preparation of palladium particles in core-shell microgels [22], or multilayered polyelectrolyte films reported recently [23]. With tetrachloropalladate a brown gel was obtained, which upon treatment with borohydride anions turned black (Fig. 1b), while with tetrachloroplatinate a yellow gel was obtained, which after reduction also turned black (Fig. 1c). The method for generation of palladium nanoparticles in the NIPAM/AUTMAB gels was the same as described above for the MEDDAB-based gels.

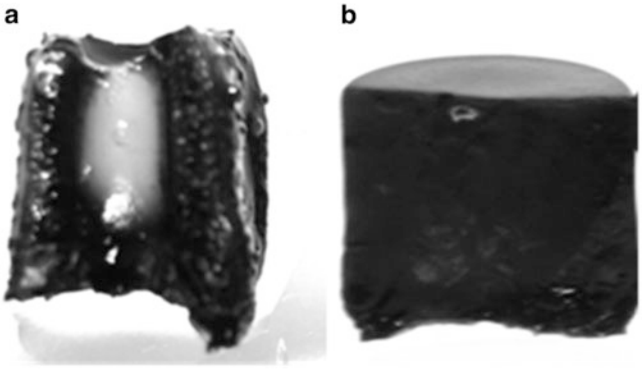


**Fig. 2** Photographic images of NIPAM/MEDDAB copolymer hydrogels functionalized with tetrachloroaurate for 24 h (**a**) and 3 weeks (**b**) and subsequent treatment with sodium borohydride

In order to determine the concentration of the metal nanoparticles at or near to the surface of the gels, EDX measurements were carried out. The N:metal ratio (atom-%) was determined after reduction of the tetrachlorometalate ions with sodium borohydride. For the gold-containing NIPAM-MEDDAB gel, the N:Au ratio was 77.3: 22.7, while for the other MEDDAB-containing gels, the N:Pd and N:Pt ratios were 97.2:2.8, i.e., the exchange of bromide for tetrachlorometalate ions was essentially complete. Also, EDX-measurements of Pd-containing NIPAM/AUTMAB hydrogels indicated a high N:Pd ratio of 97:3. Corresponding EDX spectra are shown in Fig. 3.

## Swelling Behavior of Gels Containing Metal Nanoparticles

The question now was, if the presence of the metal nanoparticles changes the reversible swelling behavior of the hydrogels. In order to answer the question, the swelling behavior of the metal-containing gels was investigated. For this purpose, the gels were immersed in 150 mL of water at 20 °C, and the weight was determined every 30 min for a time period of 8 h. Prior to weight determination the gel was put in a sieve and dried at the surface. In order to study de-swelling, the gel was kept in 150 mL of water at 50 °C and the weight decrease was determined every 30 min as described above for the swelling. For comparison, a metal-free gel was treated analogously and the swelling and de-swelling behavior was also studied. The swelling degree $S$ was determined as indicated in the Experimental part. In Fig. 4, the swelling degrees of the metal-free and metal-containing gels are plotted versus time $t$. The metal-free NIPAM-MEDDAB gel exhibits a strong swelling at 20 °C, the change in $S$, $\Delta S$, being 3.1 g/g after 8 h. The swelling is fully reversible, if the gel is kept at 50 °C. The palladium-containing NIPAM-MEDDAB gel exhibits a lower uptake of water at 20 °C, $\Delta S$ being 1.7 g/g after 8 h. It is reversible, if the gel is subsequently kept at 50 °C. Consequently the weight difference between the swollen and the shrunken state is smaller for the palladium-containing gel. For the gold and platinum-containing NIPAM-MEDDAB gels, the water uptake was even lower (Au: $\Delta S = 0.25$ g/g after 6 h; Pt: $\Delta S = 0.35$ g/g after 6 h). The reason might be that the metal nanoparticles impart hydrophobic interactions with the polymer chains in the gel so that the swelling becomes less pronounced. The metal-free NIPAM/AUTMAB hydrogels exhibit a strong swelling at 20 °C with $\Delta S$ being 5 g/g after 8 h. Again the $S$-value of the metal-containing hydrogel is much lower ($\Delta S$ being = 1.6 g/g after 8 h). If the gels are subsequently kept at 50 °C, the swelling is fully reversible.

## Morphology of Gels Containing Metal Nanoparticles

The morphology of the metal-containing gels was studied for the example of the palladium containing NIPAM/MEDDAB gel. In order to determine the size, the nanoparticles were leached out from the network. For this purpose, the gel was mechanically crushed and ultrasonicated. Subsequently the nanoparticle suspension was dropped on a copper grid with carbon net and dried. Then TEM pictures were taken at room temperature. As shown in Fig. 5a, small partially aggregated particles with average diameter of 3.6 nm can be detected. NIPAM/AUTMAB hydrogels containing $Pd^0$ nanoparticles were treated in the same manner as the metal-containing MEDDAB-based gels. In Fig. 5a, b TEM picture of the nanoparticles suspension on a copper grid with carbon net is shown. The picture was taken at room temperature. Small aggregated particles with average diameter of 5.3 nm can be detected. They are slightly larger than the particles leached out from the NIPAM/MEDDAB hydrogel.

## Catalytic Activity of Copolymer Hydrogels Containing Metal Nanoparticles

The catalytic activity of the metal-containing copolymer hydrogels was studied by investigating the reduction of 4-nitrophenol (4-NP) with sodium borohydride to yield 4-aminophenol. For mechanistic details of the process see a recent review [24]. The conversion was followed UV spectroscopically in aqueous solution by monitoring the maximum absorbance of the 4-nitrophenolate anion at $\lambda = 400$ nm.

**NIPAM/MEDDAB copolymer hydrogels**. The catalytic activity of metal-containing NIPAM/MEDDAB copolymer hydrogels was studied at 20 °C, 30 °C and 40 °C, i.e., at

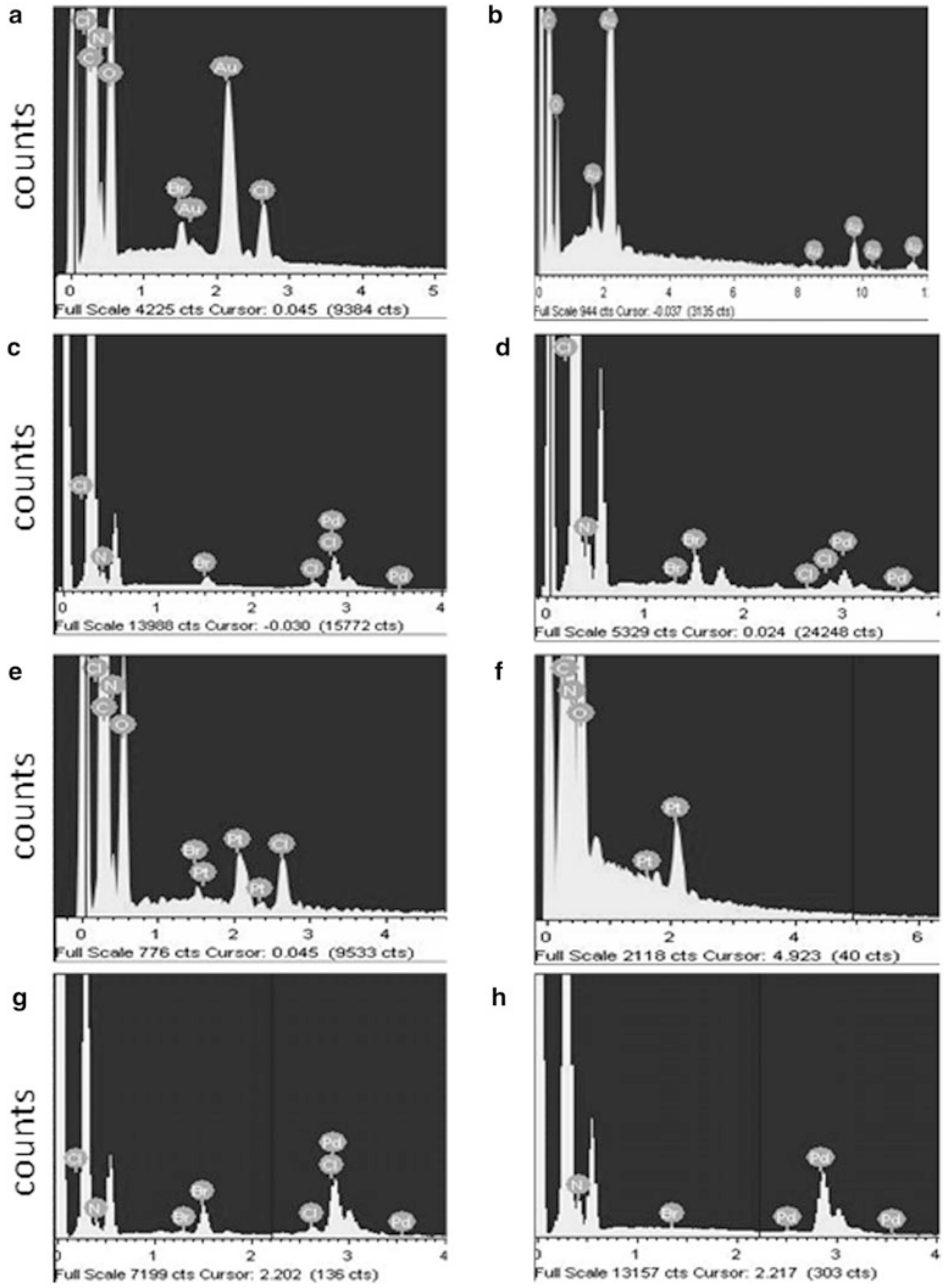


**Fig. 3** EDX measurements of a NIPAM/surfmer copolymer hydrogels after exchange of bromide for metal complex anions, and formation of metal nanoparticles. Samples: NIPAM/MEDDAB hydrogels with tetrachloroaurate (**a**), tetrachloro-palladate (**c**), and tetrachloroplatinate anions (**e**), and after formation of $Au^0$ (**b**), $Pd^0$ (**d**), and $Pt^0$ (**f**) nanoparticles, and NIPAM/AUTMAB hydrogel with tetrachloropalladate anions (**g**), and after formation of $Pd^0$ nanoparticles (**h**)

temperatures below and above the volume phase transition temperature (lower critical solution temperature, LCST) of the metal-free hydrogel at about 29 °C. Aqueous solutions of 4-NP containing hydrogels with gold, palladium, platinum, or no particles were studied. In Fig. 6, absorption spectra of 4-NP in aqueous solution of pH 7 are shown. The spectra indicate the decrease of the absorbance due to the proceeding reduction at 30 °C. For the gel without metal nanoparticles the decrease was less than 30 % even 3 h after addition of the reducing agent (Fig. 6a ). However, if metal nanoparticles are present, the reduction rate was accelerated. In presence of Pd reduction was almost complete within 80 min (Fig. 6b),while

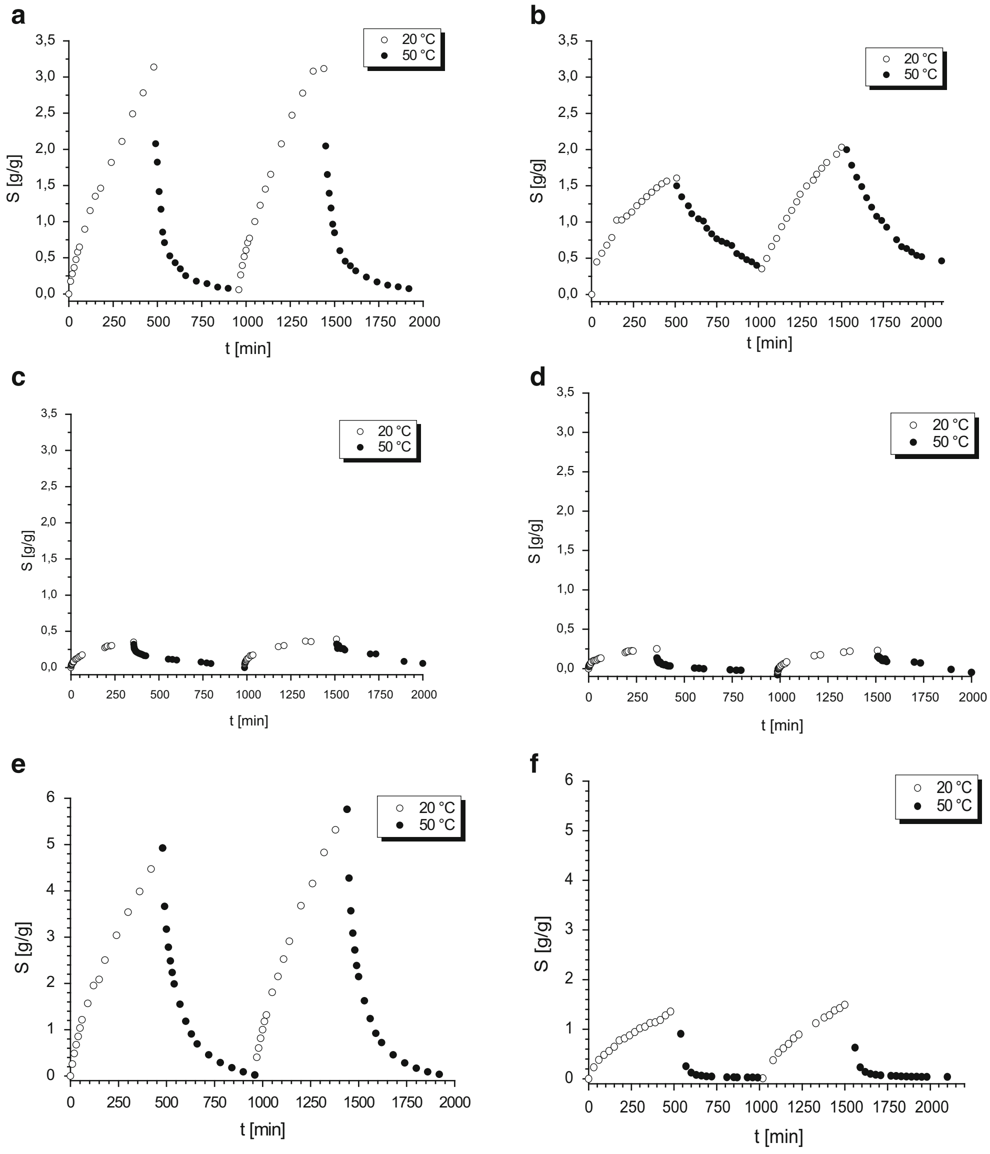


**Fig. 4** Alternate swelling at 20 °C and shrinking at 50 °C of NIPAM/surfmer hydrogels without and with metal nanoparticles. Samples: NIPAM/MEDDAB gel without (**a**), and with $Pd^0$ (**b**), $Pt^0$ (**c**), and $Au^0$ nanoparticles (**d**), and NIPAM/AUTMAB gel without (**e**), and with $Pd^0$ nanoparticles (**f**)

in presence of Au or Pt it was complete after 30 or 12 min, respectively (Fig. 6c, d). At 20 °C and 40 °C, the decrease was considerably slower (spectra are not shown).

Since sodium borohydride was added in excess, a pseudo-first order kinetics can be assumed for the reduction. In this case the conversion can be calculated using Eq. 2:

$$\ln\left(c_t/c_o\right) = \ln\left(A_t/A_o\right) = -kt \qquad (2)$$

with $c_o$ and $c_t$ being the concentration of 4-NP before and after reduction time $t$, $k$ being the rate constant, and $A_o$ and $A_t$ being the absorbance of 4-NP before and after reduction time $t$. From the linear slope in the plot of $\ln(A_t/A_o)$ versus $t$ (Fig. 7) the rate constant $k$ could be easily determined. For the catalyst-free system at 30 °C, $k$ was 0.0045 $s^{-1}$, while for the gold-, palladium- and platinum-containing gels it was 0.228, 0.051, and 0.132 $s^{-1}$, respectively.

Similar experiments were carried out at 20 °C and 40 °C. At 20 °C the rate constants were significantly lower than at 30 °C (Table 1) because counterion dissociation and osmotic pressure $\pi$ originating from the charged surfmer head groups are lower [20, 25]. With increasing $\pi$ the swelling increases and more 4-NP molecules are introduced in the gel. At 20 °C, $S$ of the metal-free gel is 2.1 g/g after 6 h swelling, while at 30 °C it is 2.5 g/g. If the reduction is carried out at 40 °C, i.e. above the LCST of the gel (LCST of the metal-free

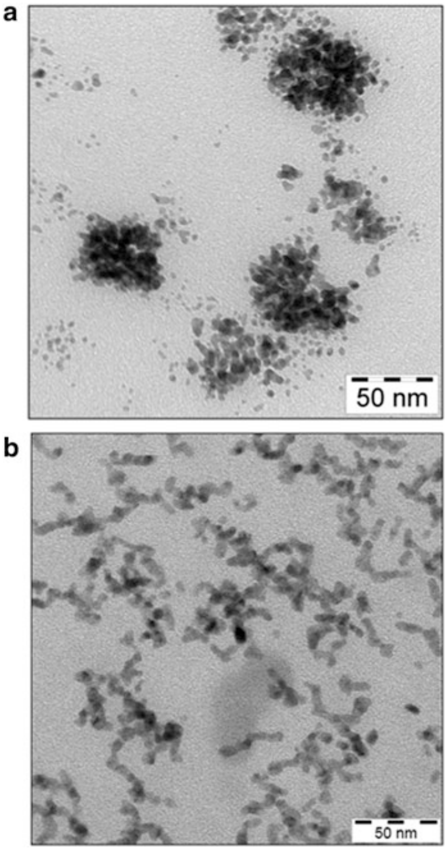


**Fig. 5** TEM image of $Pd^0$ nanoparticles of a NIPAM/MEDDAB (**a**) and a NIPAM/AUTMAB (**b**) copolymer hydrogel network

**Table 1** Rate constants *k* for reduction of 4-NP at different temperatures in presence of NIPAM/surfmer hydrogels with and without metal nanoparticles

| | | $k$ [$s^{-1}$] at | | | |
|---|---|---|---|---|---|
| Hydrogel | Metal | 20 °C | 30 °C | 40 °C | 50 °C |
| NIPAM/ MEDDAB | $Pd^0$ | 0.025 | 0.051 | 0.0048 | – |
| | $Au^0$ | 0.033 | 0.228 | 0.0071 | – |
| | $Pt^0$ | 0.032 | 0.132 | 0.0034 | – |
| | No metal | 0.0008 | 0.0045 | 0.0080 | – |
| NIPAM/ AUTMAB | $Pd^0$ | 0.016 | 0.048 | 0.064 | 0.020 |
| | No metal | 0.0009 | 0.0049 | 0.0078 | 0.022 |

gel is 29 °C), the gels are hydrophobic and shrunken, the nanoparticles are shielded by the polymer, and 4-NP cannot enter the gel. Consequently the rate constants of the metal-containing gels are very low, comparable with the metal-free gel (Table 1).

In Fig. 8a, an Arrhenius plot of the rate constants *k* versus 1/*T* is shown. Three main results are obtained. First, the metal-containing gels are catalytically active below the LCST, the activity increasing with temperature because of the increasing diffusion of the aqueous phase through the gel and improved contacts between the 4-NP molecules with the metal nanoparticles. Second, above the LCST the catalytic activity drops to the low value found for the metal-free hydrogel because the aqueous solution is expelled from the gel. The contact between 4-NP molecules and metallic nanoparticles is interrupted. Third, the catalytic activity decreases in the series Au->Pt->Pd-containing gel. The high activity of the gold-containing gel can be ascribed to the higher concentration of the gold nanoparticles as indicated by the EDX measurements (see above). The different particle concentration may originate from different interactions of the metals with the polymer matrix, metals with weak interactions being washed out more easily.

**NIPAM/AUTMAB copolymer hydrogels**. The catalytic activity of palladium-containing NIPAM/AUTMAB copolymer hydrogels was studied at 20 °C, 30 °C, 40 °C and 50 °C, i.e., below and above the LCST of the gel at 34 °C. The reaction conditions were the same as described above for the NIPAM/MEDDAB hydrogels. Again the decrease of the absorption maximum at $\lambda = 400$ nm of 4-NP at different temperatures (20 °C, 30 °C, 40 °C and 50 °C) was evaluated and $\ln(A_t/A_0)$ was plotted versus the reaction time (spectra at 30 °C are shown in Fig. 6e). Linear plots were obtained (Fig. 7e) from which the *k* values were determined (see Table 1). As for the metal-containing NIPAM/MEDDAB gels, a high rate constant *k* at 30 °C ($k = 0.048\ s^{-1}$) is found for the Pd-containing AUTMAB-based gels, but surprisingly the highest rate constant was found at 40 °C ($k = 0.064\ s^{-1}$). Small angle neutron scattering (SANS) measurements carried out previously [17] indicated a strong head group dissociation for AUTMAB in micellar aggregates, much stronger than for MEDDAB micelles. Thus the AUTMAB-containing gels exhibit a stronger osmotic pressure, which compensates the de-swelling at 40 °C, i.e., above the LCST of the metal-free gel at 33.8 °C [25]. Only at 50 °C the NIPAM/AUTMAB gels exhibit the expected decrease of *k*, because the de-swelling now dominates and 4-NP molecules are no longer in contact with the catalyst particles within the gel. In Fig. 8b an Arrhenius plot of the rate constants *k* as a function of 1/T is shown for the Pd-containing and Pd-free NIPAM/AUTMAB hydrogels. The experiment indicates that the catalytic activity is strongly related to the swelling of the gels. For charged hydrogels the swelling is both a function of their LCST and their osmotic pressure.

## Conclusions

In our study we report on the successful functionalization of NIPAM/MEDDAB and NIPAM/AUTMAB copolymer hydrogels with catalytically active metal nanoparticles.

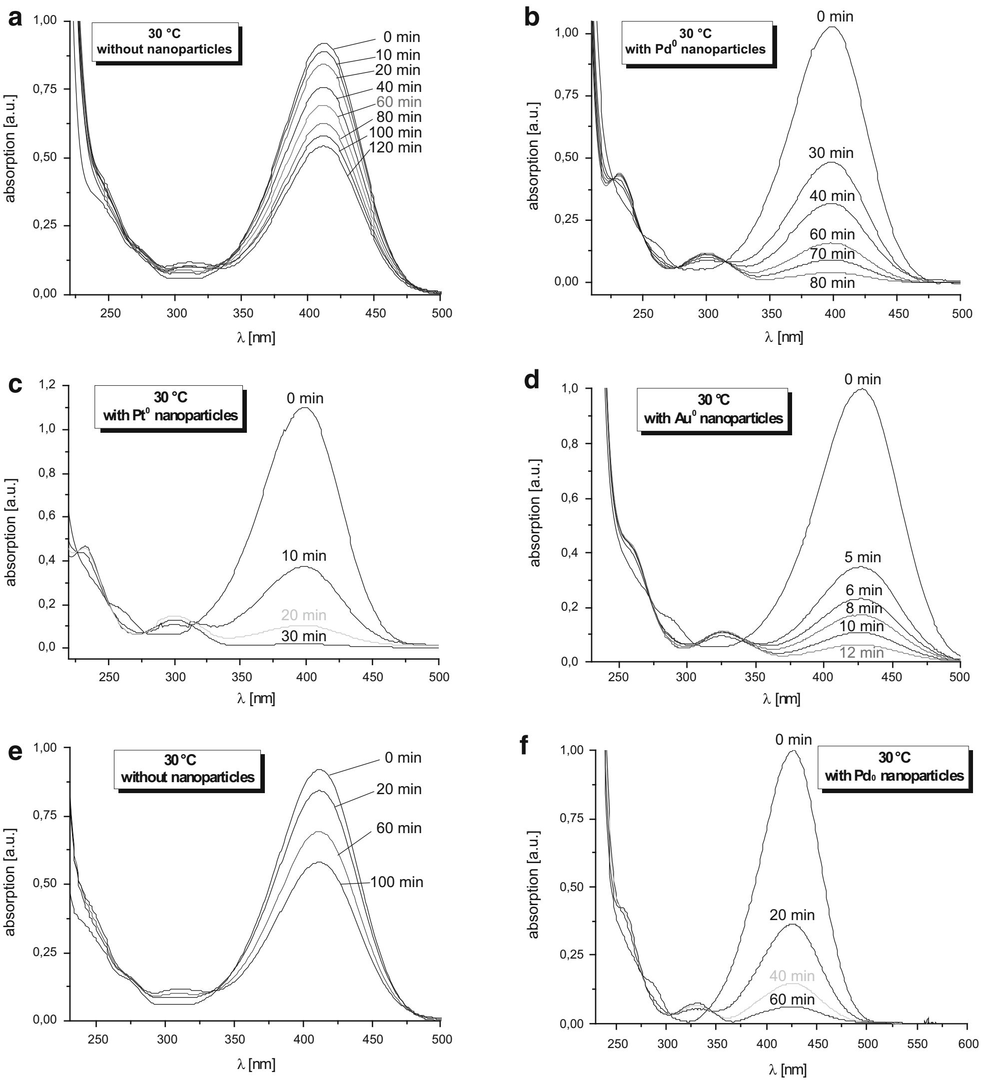


**Fig. 6** Reduction of 4-nitrophenol with excess $NaBH_4$ in presence of NIPAM/surfmer hydrogels with and without metal nanoparticles. Samples: NIPAM/MEDDAB hydrogels without (**a**), and with $Pd^0$ (**b**), $Pt^0$ (**c**) or $Au^0$ nanoparticles (**d**), and NIPAM/AUTMAB hydrogel without (**e**) and with $Pd^0$ nanoparticles (**f**). Reaction conditions: $[4\text{-NP}] = 0.05$ mmol/L, $[NaBH_4] = 5$ mmol/L, T = 30 °C

Gold, platinum and palladium particles of approximately 3–5 nm in size could be prepared in-situ upon reduction of inorganic complex anions with sodium borohydride. The formation was proven by UV spectroscopy, EDX- and TEM-measurements.

The catalytic activity of the metal nanoparticles was demonstrated by studying the reduction of 4-nitrophenol with an excess of sodium borohydride. It was found that the catalytic activity is strongly controlled by the hydrophilicity of the NIPAM/surfmer-based copolymer gels. The hydrophilicity depends on the volume phase transition temperature, and the osmotic pressure of the gels. Below the phase transition temperature the gels are highly swollen and 4-NP molecules can easily diffuse through the gel and become reduced. Above the phase transition a penetration into the gel is rendered difficult, the gels are hydrophobic and the aqueous 4-NP solution is expelled from the gel, the catalyst is shielded by the polymer. The only exception is a high osmotic pressure originating from a strong head group dissociation, which may compensate the loss in hydrophilicity above the LCST in a small temperature range. This behavior was observed for the NIPAM/AUTMAB gels.

The catalytic activity of the gold containing NIPAM/MEDDAB gels was highest because more gold than platinum or palladium nanoparticles could be prepared in the gel. The reason might be that these particles are better fixed to the gel matrix via coordinative interactions. Due to interactions with the gel matrix the metal particles were generally leached out from the gels rather slowly so that the gels could be repeatedly used for reduction experiments. Because of their excellent properties the metal nanoparticle-containing hydrogels are well suited for catalytic applications.

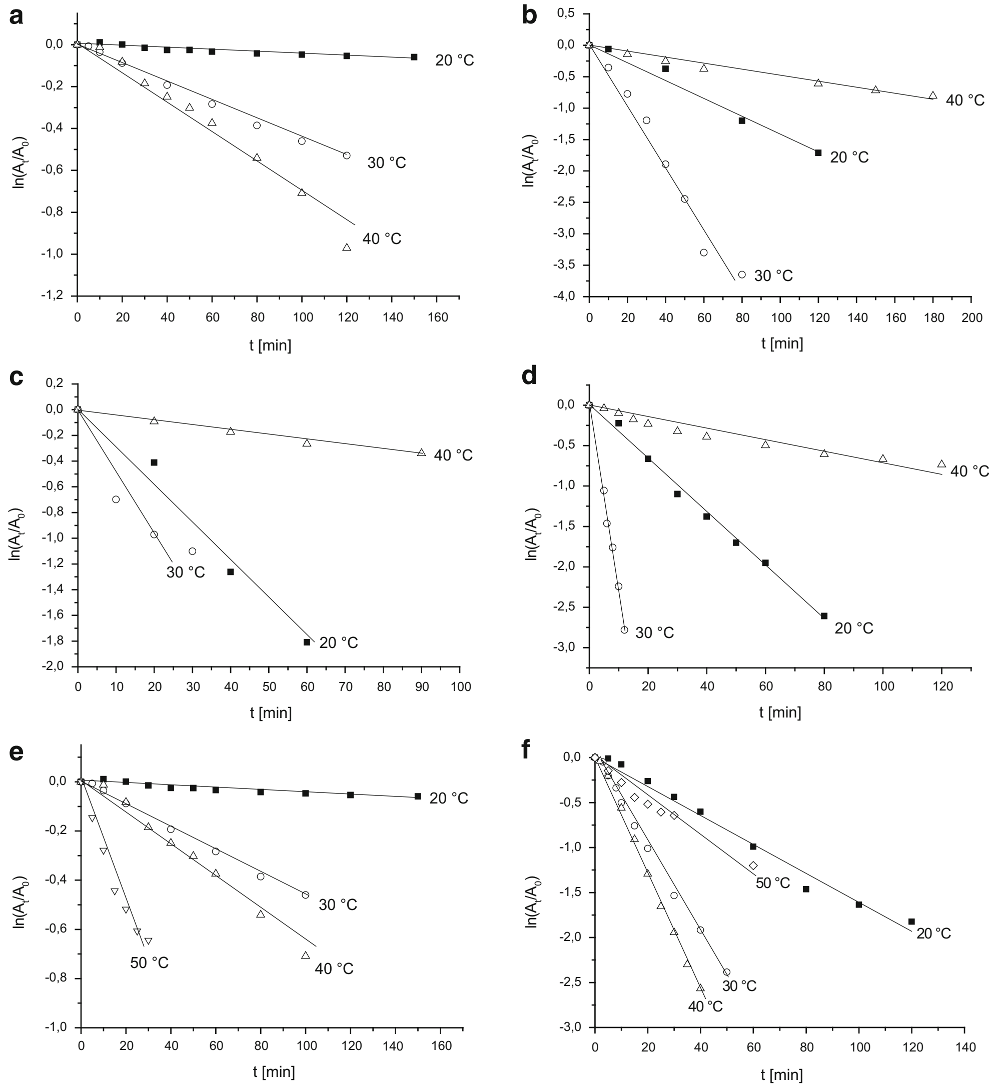


**Fig. 7** Plot of ln($A_t/A_o$) versus time for reduction of 4-nitrophenol with excess $NaBH_4$ in presence of NIPAM/surfmer hydrogel at different temperatures. Samples: NIPAM/MEDDAB hydrogel without (**a**), and with $Pd^0$ (**b**), $Pt^0$ (**c**) or $Au^0$ nanoparticles (**d**), and NIPAM/AUTMAB hydrogel without (**e**) and with $Pd^0$ nanoparticles (**f**). Reaction conditions: [4-NP] = 0.05 mmol/L, [$NaBH_4$] = 5 mmol/L. *Solid lines* are linear fits through the experimental points

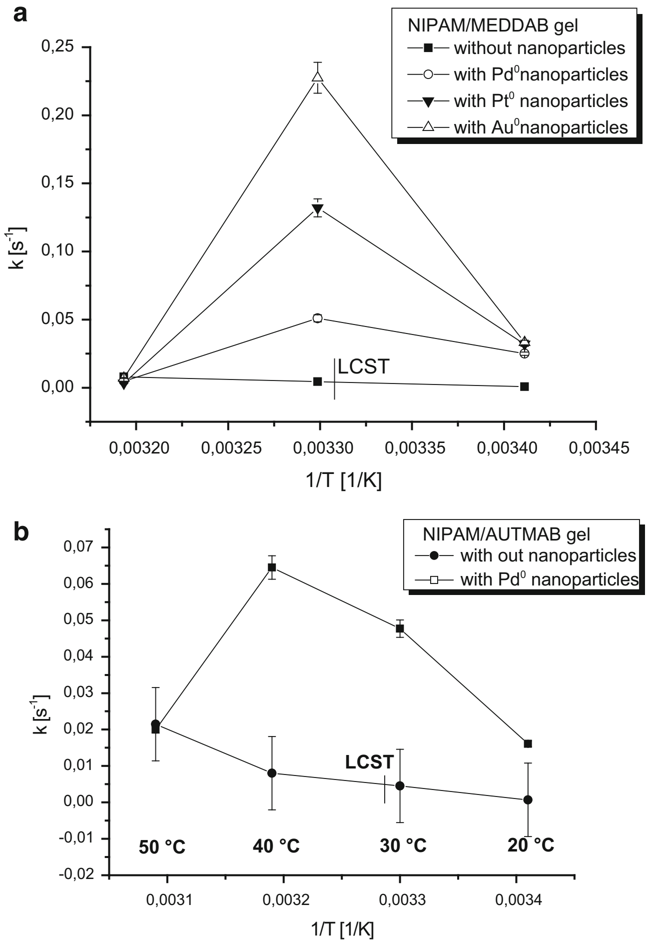


**Fig. 8** Arrhenius plot of the rate constant *k* versus 1/*T* for reduction of 4-nitrophenol with $NaBH_4$ in presence of NIPAM/surfmer hydrogels with and without metal nanoparticles. Samples: NIPAM/MEDDAB gels (**a**), and NIPAM/AUTMAB gel (**b**). Reaction conditions: [4-NP] = 0.05 mmol/L, [$NaBH_4$] = 5 mmol/L. The LCSTs of the metal-free gels are indicated. *Solid lines* are connections of the data points

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