Functionalization of Hydrogels Based on *N*-Isopropyl-acrylamide and Cationic Surfactant Monomers upon Electrostatic Self-Assembly

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Summary: Positively charged copolymer hydrogels based on N-isopropyl-acrylamide (NiPAAm) and a cationic surfactant monomer (surfmer) were functionalized upon electrostatic self-assembly of functional organic or inorganic complex counterions in the gel. As cationic surfmers 11-acryloylundecyltrimethylammonium bromide (AUTMAB) or 11-methacryloyl-undecyltrimethylammonium bromide (MUTMAB) were used. The hydrogels were prepared from a micellar aqueous solution of the surfmer and NiPAAm either upon ^{60}Co-gamma irradiation, or upon chemical cross-linking using methylenebisacrylamide as cross-linker and 1,4-diaminobutane as accelerator. Electrostatic self-assembly was facilitated utilizing the thermoresponsive swelling and shrinking of the hydrogel. Several examples of gel functionalization are described such as in-situ preparation of Prussian Blue and Pd^0 nanoparticles, and induction of fluorescent properties. The catalytic activity of the palladium-containing gel was studied by investigating the reduction of 4-nitrophenol (4-NP) with sodium borohydride as a model reaction. Fluorescent gels can be prepared upon exchange of bromide against 1-pyrenesulfonate ions in the gel.

Keywords: catalyst; hydrogel; *N*-isopropylacrylamide; self-assembly; surfactant

Introduction

The exchange of counterions in charged hydrogels represents an easy way to tailor the chemical and physical gel properties at the molecular level. For example, hydrogels containing acrylic or maleic acid were functionalized by introducing metal ions,[1,2,3] or cationic dyes.[4,5,6] Due to incorporation of functional counterions, gels may become interesting for technical applications in the fields of sensors, actuators, switches, drug delivery and catalysis. Recently we reported on thermoresponsive hydrogels prepared upon micellar copolymerization of N-isopropylacrylamide (NiPAAm) and cationic surfactant monomers (surfmers) in a one-step reaction.[7,8] Hydrogel networks with fixed positive charges were obtained, the charges being counterbalanced by bromide counterions. As recently demonstrated, the copolymer hydrogels show high and reversible swelling behaviour[7] and improved mechanical stability.[9]

Aim of the present work is to briefly review our recent activities on modification of the NiPAAm/surfmer-based copolymer gels upon electrostatic self-assembly of negatively charged functional ions. The self-assembly approach is suitable for gels containing thermosensitive P-NiPAAm, which rapidly shrinks above its lower critical solution temperature (LCST) and swells at temperatures below the LCST. As will be shown in the following, the thermoresponsive behaviour is excellently suited for introduction of a variety of counterions exhibiting strongly UV/Vis-absorbing and emitting properties, catalytically active sites, or nanoparticles in the gel. While the present article briefly describes a few

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examples of gel functionalization, detailed reports on luminescent modification of the gel, and the introduction of catalytic activity will be published in the near future.[10,11]

Experimental Part

Materials

11-Acryloyloxyundecyltrimethylammonium bromide (AUTMAB) and 11-methacryloyloxyundecyltrimethylammonium bromide (MUTMAB) were synthesised according to the literature.[7] N-Isopropylacrylamide (NiPAAm) (Acros) was recrystallized from toluene and n-hexane (volume ratio: 1: 2). Milli-Q-water was used for all experiments. All other chemicals were used without further purification.

Preparation of Hydrogels

Hydrogel samples were prepared in quartz cuvettes or screw-capped glass tubes at 20 °C. Monomer solutions containing 10% (w/w) NiPAAm and 1% (w/w) AUTMAB or 2% (w/w) MUTMAB in degassed Milli-Q-water were homogenized using a Vortex mixer, aged for 24 hours and subsequently copolymerized in a one-step reaction. AUTMAB/NiPAAm gels were polymerized using ^{60}Co-gamma-radiation, the dose rate being 128.3 Gy/h, the radiation dose being 80 kGy.[7] MUTMAB/NiPAAm gels were prepared upon radical polymerization using 0.1% (w/w) potassium peroxodisulfat as initiator, 0.15% (w/w) tetramethylenediamine (TEMED) as accelerator and 0.15%(w/w) N,N′-methylenebisacrylamide (BIS) as cross-linker as known from the literature.[12,13]

Exchange of Counterions

For exchange of bromide counterions the thermoresponsive swelling and shrinking of the gels was used as outlined in Scheme 1.[10] Gels were shrunken at 50 °C for 8 hours and subsequently re-swollen at 20 °C in an aqueous solution of the new counterions for 48 hours. The concentration was 1 mM for solutions containing Na_2PdCl_4 and sodium 1-pyrenesulfonate and 10mM for the aqueous solution of $K_3[Fe(CN)_6]$. This process was followed by two shrinking/re-swelling cycles in Milli-Q-water to leach out excess anions, not electrostatically bound to the surfmers.

Preparation of Prussian Blue Containing Hydrogels

$[Fe(CN)_6]^{3-}$ containing hydrogels were shrunken at 50 °C for 8 hours and subsequently re-swollen at 20 °C in an aqueous solution of 10 mM $(NH_4)_2Fe(SO_4)_2$ for 48 hours, followed by two shrinking/re-swelling cycles in Milli-Q-water.

Preparation of Pd^0 Containing Hydrogels

$PdCl_4^{2-}$ containing hydrogels were shrunken at 50 °C for 8 hours and subsequently re-swollen at 20 °C in an aqueous solution of 13 mM $NaBH_4$ for 48 hours, followed by two shrinking/re-swelling cycles in Milli-Q-water.

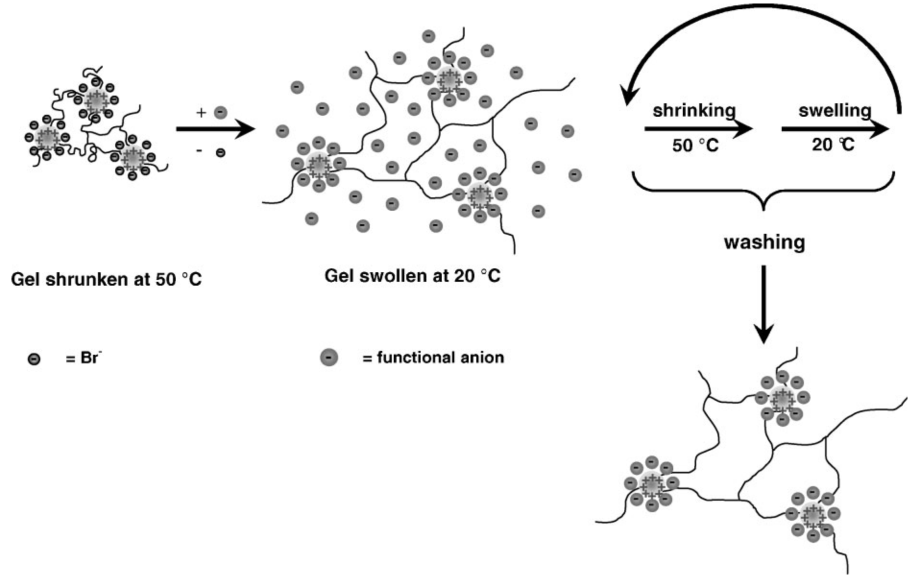
Methods

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy were performed using the Zeiss Neon 40 SEM equipped with an Inca Dry Cool EDX detector for microanalysis. Hydrogel samples were dried in vacuum at room temperature, fixed to the microscope holder using conductive silver paste, and coated with carbon (EMITECH K950X). The software Inca was used for EDX analysis. The experimental error of the EDX measurements is about 5% of the measured value.

UV/VIS absorption spectra were recorded using a Perkin-Elmer Lambda 14 spectrometer. All spectra were corrected by subtracting the background signal.

Results and Discussion

The copolymer hydrogels used in our study were obtained upon polymerization of aqueous micellar solutions containing NiPAAm and either 11-acryloylundecyltrimethylammonium bromide (AUTMAB), or 11-methacryloylundecyltrimethylammonium bromide (MUTMAB). Polymeriza-



Scheme 1.
Structure model of electrostatic self-assembly of functional ions.

tion was carried out upon ^{60}Co-gamma-irradiation or radical polymerization. Gamma irradiation was chosen because no additives such as cross-linker and accelerator are needed, and the polymerization can be carried out at room temperature. Due to copolymerization with the cationic surfmers, the hydrogels were positively charged, the charges being located at the surface of the copolymerized micelles (Scheme 1).

Functional properties were introduced by replacing the bromide counterions of the surfmers for a variety of functional anions upon electrostatic self-assembly utilizing the thermoresponsive shrinking and swelling of the gels as described in detail in the Experimental section.

Prussian Blue Containing Hydrogels

As a first example we studied the in-situ formation of Prussian Blue (PB) nanoparticles in the gel (Figure 1a). The procedure used for PB preparation was derived from the preparation of ultrathin PB films upon multiple sequential adsorption of hexacyanoferrate(III) and iron(II) ions reported recently.[14,15]

First, a shrunken hydrogel containing 1% (w/w) AUTMAB and 10% (w/w) NiPAAm was re-swollen in an aqueous solution of $K_3[Fe(CN)_6]$. After leaching out non-bound anions a brownish yellow hydrogel containing the $[Fe(CN)_6]^{3-}$ ions was obtained. Second, the hydrogel was subjected to a shrinking/swelling cycle in an aqueous solution of $(NH_4)_2Fe(SO_4)_2$ to yield a deep blue gel containing fixed PB particles (Figure 1a). Energy dispersive X-Ray (EDX) measurements indicated that all bromide counterions in the gel were replaced for $[Fe(CN)_6]^{3-}$ anions during the counterion exchange. Furthermore the iron content was analyzed, the atomic ratio of N: Fe was found to be 4: 1.

Hydrogels Containing Pd^0 Nanoparticles

For the preparation of catalytically active hydrogels containing Pd^0 nanoparticles, a method previously used for palladium formation in spherical polyelectrolyte brushes,[16] core-shell microgels,[16] and polyelectrolyte multilayer assemblies[17] was applied. Shrunken hydrogels containing 2% (w/w) MUTMAB and 10% (w/w) NiPAAm were first re-swollen in an aqu-

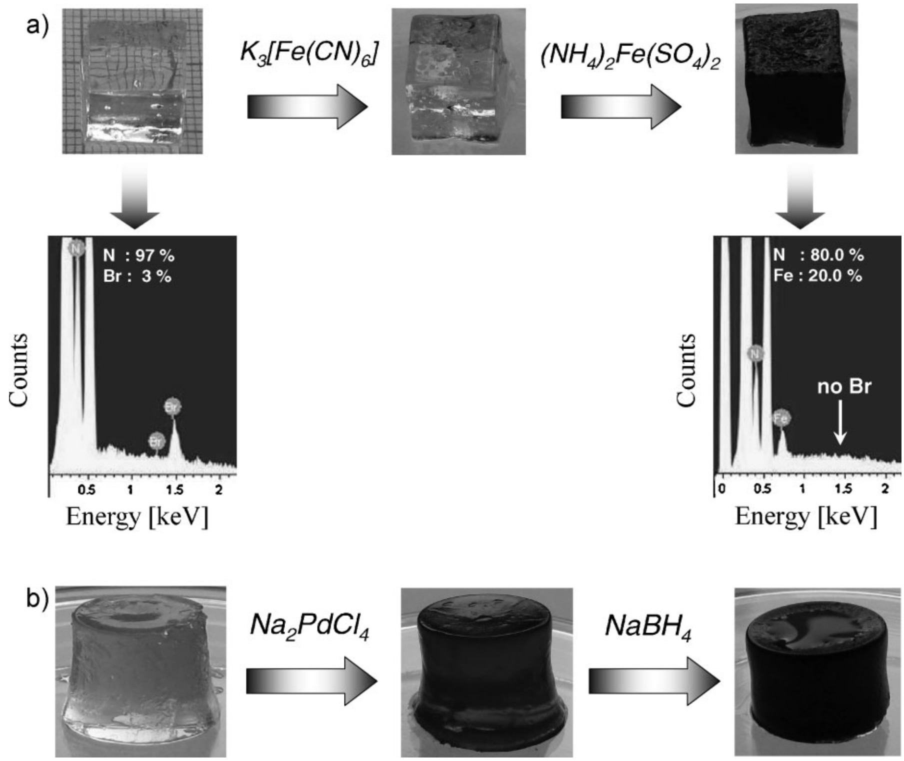


Figure 1.

(a) AUTMAB/NiPAAm-copolymer hydrogel before (left) and after electrostatic adsorption of $[Fe(CN)_6]^{3-}$ anions (mid) and treatment with $(NH_4)_2Fe(SO_4)_2$ to yield Prussian Blue nanoparticles in the gel (right). EDX measurements of the hydrogel prior and after functionalization are also shown. (b) MUTMAB/NiPAAm-copolymer hydrogel before (left) and after electrostatic adsorption of tetrachloropalladate anions (mid) and treatment with sodium borohydride to yield Pd^0 nanoparticles in the gel (right).

eous solution of sodium tetrachloropalladate to yield a brownish gel (Figure 1b). Subsequently the gels were shrunken again and re-swollen in an aqueous solution containing sodium borohydride. The borohydride anions reduced the $PdCl_4^{2-}$ ions resulting in the formation of Pd^0 nanoparticles. This process could be easily followed by a colour change of the gel from brown to black (Figure 1b).

Scanning electron microscopy (SEM) was used to study the surface morphology of the hydrogels. A large amount of Pd^0 particles was found indicating an accumulation of the nanoparticles in the surface-near region of the hydrogel (Figure 2).

The structure of the hydrogels was studied using transmission electron microscopy (TEM). TEM was performed using the freeze fracture direct imaging method. Nanoparticles of about 6 nm in diameter were found, which were distributed homogeneously in the network.[11]

In order to determine the concentration of Pd^0 particles, EDX measurements were carried out. Inside the gel a N: Pd ratio (atom-%) of 99.8: 0.2 was found, whereas at the surface the ratio was 71.8: 28.2. A hydrogel containing $PdCl_4^{2-}$ counterions was also investigated. Inside the gel, the N: Pd ratio was 98.5: 1.5, and at the surface 84.2: 15.8. Two reasons may be responsible for the accumulation of Pd^0-nanoparticles in the surface-near region. First, the Pd^0 particles formed upon reduction are no longer electrostatically fixed in the gel,

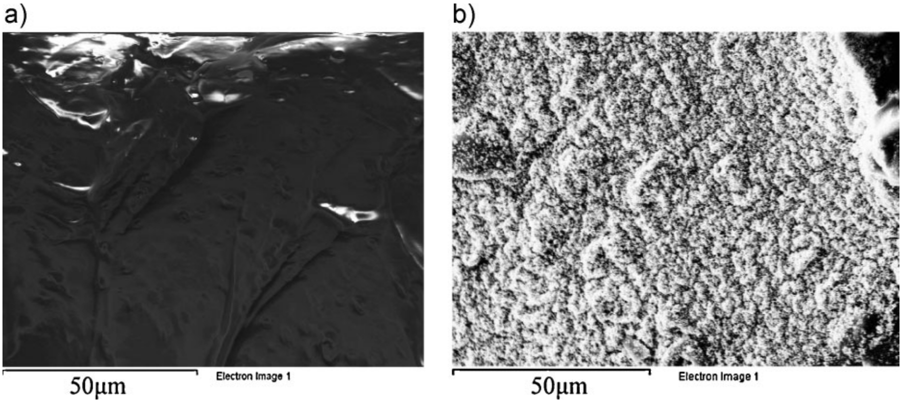
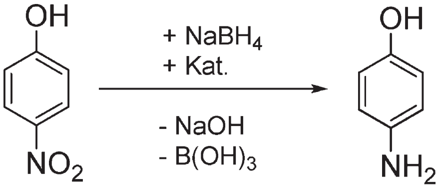


Figure 2.
SEM pictures of NiPAAm/MUTMAB copolymer hydrogel containing 10% NiPAAm and 2% MUTMAB without (a) and with Pd-nanoparticles (b).

diffuse through the gel and are concentrated in the outer gel region. This may explain why the gels containing $PdCl_4^{2-}$ anions exhibit a higher Pd concentration inside the gel than the gels containing the Pd^0 nanoparticles. Second, a skin effect may occur, which causes that $PdCl_4^{2-}$ anions adsorbed in the surface region render the diffusion of further anions into the interior of the gel difficult for steric and for electrostatic reasons.

The catalytic activity of Pd^0-containing MUTMAB/NiPAAm hydrogels was studied by investigating the reduction of 4-nitrophenol (4-NP) with sodium borohydride (Scheme 2) at temperatures below and above the LCST, and at the LCST (32 °C) of the copolymer gel. The Pd^0 containing hydrogels were re-swollen to their original size in Milli-Q-water prior to the experiments. For comparison the reaction was also studied in a catalyst-free system. The reduction was followed by monitoring the time-dependent decrease of the absorbance A of 4-nitrophenol at 405 nm.



Scheme 2.
Reduction of 4-nitrophenol with sodium borohydride.

In Figure 3, UV/Vis measurements are shown for the reaction at 20 °C. Since sodium borohydride was used in excess, a pseudo-first order reaction can be assumed for the reduction of 4-nitrophenol, and the conversion can be calculated using Eq. 1:

$$\ln\frac{c_0}{c_t} = \ln\frac{A_0}{A_t} = k \cdot t \tag{1}$$

with c being the concentration of 4-nitrophenol and k being the rate constant. From the plot of $\ln(A_0/A_t)$ versus t it was possible to determine k from the slope of the line fitted through the data points.

In Figure 4 the determination of the rate constants of the catalytic reduction are shown. The highest rate constants were obtained at 40 and 20 °C. In Figure 5 the Arrhenius plots for the reduction in presence or absence of the Pd^0-containing gel are shown. At low temperature the rate constants were quite different. At 20 °C, k was $0.1864\,s^{-1}$ in presence and $7 \cdot 10^{-4}$ in absence of the gel.

This clearly demonstrates a catalytic effect of the Pd^0 nanoparticles in the hydrogel. At 40 °C, the rate constants were the same, no matter if the Pd^0-containing hydrogel was present or not. The reasons for this behaviour are (a) the temperature-

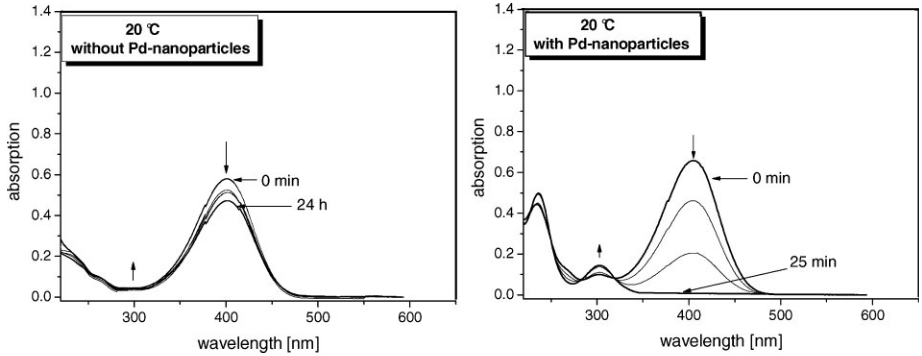


Figure 3.
Reduction of 4-nitrophenol with excess $NaBH_4$ with and without presence of Pd^0 containing hydrogel at 20 °C. Reaction condition: [4-NP] = 0,05 mmol/l, $[NaBH_4]$ = 5 mmol/l.

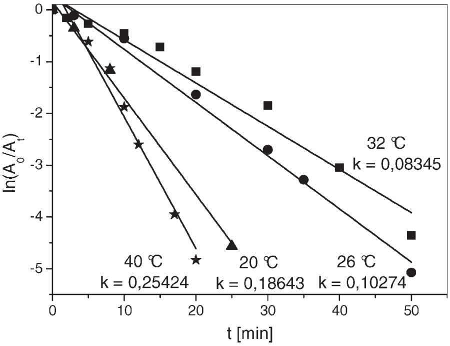


Figure 4.
Plot of $\ln(A_0/A_t)$ vs. time for reduction of 4-nitrophenol at different temperatures in presence of Pd^0-containing hydrogel. Reaction condition: [4-NP] = 0.05 mmol/l, $[NaBH_4]$ = 5 mmol/l.

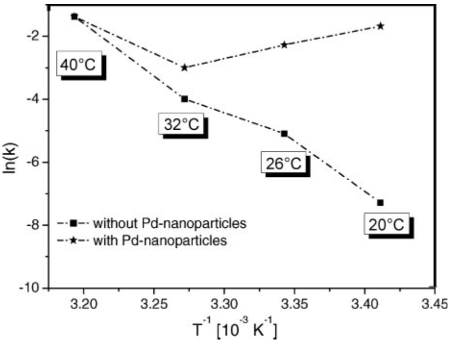


Figure 5.
Arrhenius plot of the rate constant *k* for the reduction of 4-nitrophenol. Reaction condition: [4-NP] = 0.05 mmol/l, [NaBH4] = 5 mmol/l.

dependence of *k*, and (b) the temperature-sensitive behaviour of the functionalized hydrogel. At temperatures above the LCST the gel network becomes hydrophobic, the aqueous solution of 4-nitrophenol is expelled from the gel, and the catalytically active Pd^0 nanoparticles are shielded by the polymer. At temperatures below the LCST the hydrogels are hydrophilic and swollen in the solution. During swelling, 4-nitrophenol molecules are able to enter the NiPAAm/MUTMAB hydrogel, where they are reduced by the Pd^0-nanoparticles. The rate constant of the catalytic reduction at 26 °C is smaller than the value obtained at 20 °C. This might be caused by the gradual onset of the volume transition restricting the diffusion in the network.

Fluorescent Hydrogels

Fluorescent AUTMAB/NiPAAm hydrogels were prepared upon electrostatic self-assembly of 1-pyrenesulfonate anions as outlined in Scheme 1.[10] For this purpose the shrunken hydrogel was re-swollen in an aqueous solution containing sodium 1-pyrenesulfonate. As shown in Figure 6, the gels exhibit a blue fluorescence.

Quantitative UV/Vis studies indicated that the amount of adsorbed 1-pyrenesulfonate was proportional to the amount of surfmer copolymerized in the gel. EDX measurements indicated that 20% of the bromide counterions were replaced by the

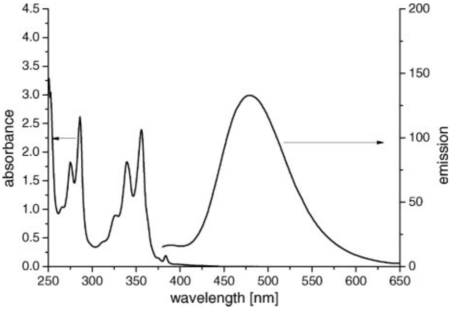


Figure 6.
UV/VIS- and fluorescence spectra of a NiPAAm/AUTMAB hydrogel containing 10% (w/w) NiPAAm and 1% (w/w) AUTMAB after electrostatic adsorption of 1-pyrenesulfonate. Excitation at 340 nm.

fluorescent counterions.[10] Furthermore it could be demonstrated that the pyrene-based counterions can be released again, if the hydrogel is immersed in acidified water. At a pH of 1, almost the total amount of the fluorescent compound is set free.

Conclusion

In our contribution, we report an easy method to functionalize positively charged NiPAAm/surfmer copolymer hydrogels upon electrostatic self-assembly of functional anions utilizing the thermoresponsive swelling/shrinking behaviour of the gels. The exchange process is first of all driven by the concentration gradient of the ions between solution and gel. In addition, differences in charge density, hydrophilicity and shape of the present ions may also play a role. Using the exchange reaction, hydrogels with a variety of functional properties can be easily prepared. For example, the in-situ preparation of inorganic nanoparticles is possible. Hydrogels containing Prussian Blue, or catalytically active Pd^0 particles are described. For the palladium-containing gel, an application as catalyst for hydrogenation is demonstrated. Electrostatic adsorption of organic functional ions such as 1-pyrenesulfonate enables the formation of fluorescent gels. Other inorganic nanoparticles, for example magnetite, gold or titanium dioxide particles may be introduced, or enzymatically active hydrogels may be prepared. Since the adsorbed ions can be released again, further application of the NiPAAm/surfmer copolymer gels in the area of controlled drug release seems feasible.

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[1] I. Katime, E. Rodriguez, *J. Macromol. Sci. A* **2001**, *38*, 543.
[2] D. Saraydin, E. Karada, O. Güven, *Sep. Sci. Technol.* **1995**, *30*, 3287.
[3] W. Li, H. Zhao, P. R. Teasdale, R. John, S. Zhang, *React. Funct. Polym.* **2002**, *52*, 31.
[4] S. Duran, D. Solpan, O. Güven, *Nucl. Instr. Meth. Phys. Res. B* **1999**, *151*, 196.
[5] E. Karada, Ö. B. Üzüm, D. Saraydin, *Eur. Polym. J.* **2002**, *38*, 2133.
[6] Ö. B. Üzüm, E. Karada, *Adsorption* **2006**, *12*, 77.
[7] T. Friedrich, B. Tieke, M. Meyer, W. Pyckhout-Hintzen, V. Pipich, *J. Phys. Chem. B* **2010**, *114*, 5666.
[8] T. Friedrich, B. Tieke, *Macromol. Symp.* **2010**, *287*, 16.
[9] T. Friedrich, B. Tieke, F. Stadler, Ch. Bailly, *submitted.*
[10] T. Friedrich, B. Tieke, *Colloid Polym. Sci.* **2010**, DOI: 10.1007/s00396-010-2270-2.
[11] A. Trinker, T. Friedrich, B. Tieke, *to be published.*
[12] Y. Hirokawa, T. Tanaka, *J. Chem. Phys.* **1984**, *81*, 6379.
[13] D. K. Akta, Ö. Pekcan, *Phase Transitions* **2006**, *79*, 921.
[14] M. Pyrasch, B. Tieke, *Langmuir* **2001**, *17*, 7706.
[15] M. Pyrasch, A. Toutianoush, W. Jinn, J. Schnepf, B. Tieke, *Chem. Mater.* **2003**, *15*, 245.
[16] Y. Mei, Y. Lu, F. Polzer, M. Ballauf, M. Drechsler, *Chem. Mater.* **2007**, *19*, 1062.
[17] S. Kidambi, M. L. Bruening, *Chem. Mater.* **2005**, *17*, 301.