Intelligent Hydrogels Via Gamma-Ray Induced Polymerization of Micellar Monomer Solutions and Microemulsions

*Tatjana Friedrich, Bernd Tieke**

Summary: Intelligent hydrogels were prepared upon polymerization of micellar aqueous comonomer solutions and microemulsions containing the cationic surfactant monomer 11-acryloyloxyundecyltrimethylammonium bromide (AUTMAB) and N-isopropylacrylamide (NIPAM). A chemically and physically cross-linked network structure is formed consisting of blocks of P-NIPAM and P-AUTMAB. The P-AUTMAB blocks act as physical cross-linking units improving the mechanical stability of the gel. While pure P-NIPAM hydrogels are disrupted under low compression, gels polymerized from micellar solution or microemulsion can be reversibly compressed. The presence of AUTMAB in the gel increases the swelling up to a factor of 30 compared with the pure P-NIPAM gel. Rapid and reversible swelling is observed for hydrogels with an AUTMAB content up to 2.5 wt.-%.

Keywords: thermosensitive hydrogel; surfmer; micelles; swelling; poly(N-isopropylacrylamide)

Introduction

Poly(N-isopropylacrylamide) (P-NIPAM) hydrogels are known to undergo a reversible phase transition from water-soluble to insoluble, if heated to temperatures above 32 °C, the lower critical solution temperature (LCST) of the gel. The phase transition involves clouding of the hydrogel network and expulsion of incorporated water. Reversibility of the transition renders the hydrogels attractive for sensor applications or controlled drug release, for example. Remarkable disadvantages of many intelligent gels are mechanical weakness, limited swelling and shrinkage, and a slow response to external stimuli.

Our work is aimed at the preparation of new, mechanically stable and intelligent hydrogels in a one-step reaction using gamma-ray induced polymerization of micellar aqueous comonomer solutions and microemulsions containing a surfactant monomer (surfmer) and NIPAM.

The micelles act as physical cross-linking units (Figure 1) improving the mechanical stability of the hydrogel. Furthermore, the hydrophobic core can be used to solubilize organic molecules such as fluorescent dyes or magnetic nanoparticles introducing functional properties in the hydrogels. Presence of surfactant might also influence LCST, swelling and shrinking of the P-NIPAM hydrogels.

Up to now, only few studies on P-NIPAM hydrogels containing a surfmer or an amphiphilic polymer were reported.[1–4] In most studies, gels were prepared upon chemically-induced free radical polymerization, and the reaction was carried out as a two-step process by first polymerizing the surfmer followed by NIPAM polymerization[2,3], or first preparing a linear NIPAM-surfactant copolymer followed by cross-linking.[1] Our project differs from previous work in that a radiation-induced one-step method is used, in which a clear aqueous

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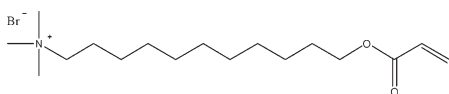tatjana.friedrich@uni-koeln.de

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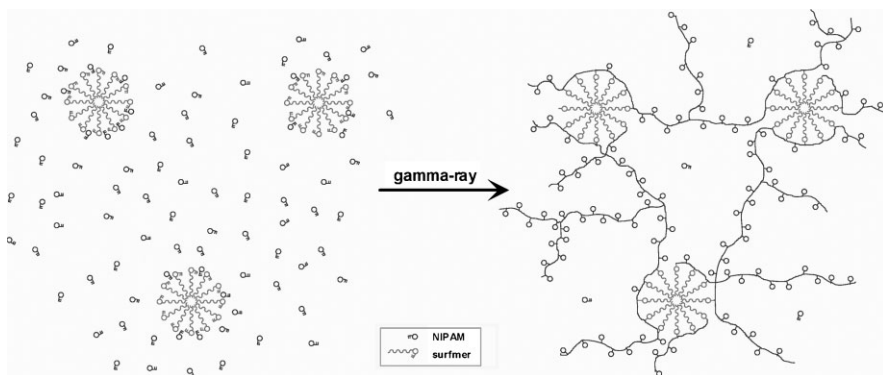
Figure 1.
Structure model of the polymerization in aqueous micellar surfmer/NIPAM-solution.
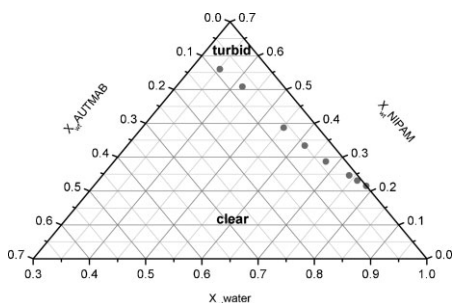
monomer solution is transferred into a clear hydrogel upon gamma-irradiation. Here we present a first study on hydrogels containing the cationic surfmer 11-acryloylundecyl-trimethylammonium bromide AUTMAB (Figure 2) and NIPAM.

Results and Discussion

For the preparation of clear, homogeneous hydrogels a clear single phase monomeric solution or microemulsion is needed. To obtain information about the existence of single phase regions, a detailed study of the phase behaviour of micellar surfmer solutions was carried out. In addition, micro-emulsions containing styrene as polymerizable oil component were also studied. In Figure 3 a partial phase diagram of the system NIPAM/AUTMAB/water at 20 °C is shown. It can be seen that with increasing amount of solubilized surfactant the solubility of NIPAM and the transparent single phase area increase. In Figure 4, corresponding partial phase diagrams of the systems AUTMAB/styrene/water and NIPAM/AUTMAB/styrene/water at 20 °C are shown. A comparison of the phase

Figure 3.
Partial phase diagram of the system AUTMAB/NIPAM/water indicating the clear/turbid-boundary of the micellar solution (T = 20 °C).
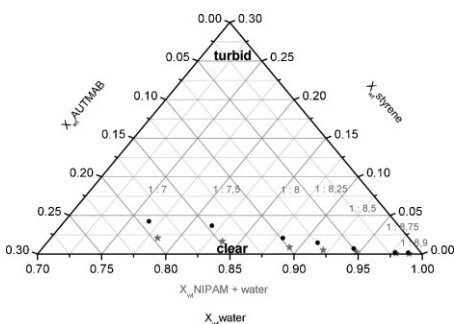
Figure 4.
Partial phase diagram of the systems AUTMAB/styrene/water and AUTMAB/NIPAM/styrene/water indicating the clear/turbid-boundary of the microemulsions (T = 20 °C). NIPAM: water ratios are indicated.

Figure 2.
Molecular structure of AUTMAB.

behaviour of the two systems indicates that the solubility of styrene in the micelles increases, if the surfactant concentration is increased. However, if NIPAM is present in the system, the styrene solubilization in the AUTMAB micelles is generally much lower. This points to an assembly of NIPAM in the micelles.

Structure studies of the aqueous monomer solutions and microemulsions were carried out using small angle neutron scattering. Particle sizes determined by means of Guinier approximation are given in Table 1. The SANS measurements indicate that styrene is solubilized in the micelles and thereby the size is increased (Figure 5), while the addition of NIPAM leads to smaller particles. This effect can be ascribed to the incorporation of NIPAM molecules in the shell of the AUTMAB-micelles (Figure 5), which increases the curvature and decreases the size of the micelles. As a consequence of the reduced size, less styrene is incorporated in the micelles. An increase of the AUTMAB concentration has no effect on the size of micelles, and the influence of temperature on the size of the micelles is only small.

Polymerization was initiated upon gamma-irradiation. High energy radiation is able to homogenously penetrate the sample avoiding possible inequalities of the gel. There is no need to add initiators or crosslinkers, which later on often cause inhomogenities and turbidity of the hydrogel network. Since radiation-induced polymerization can be carried out at room
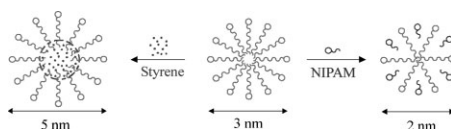

Figure 5.
Self-assembly of NIPAM in the shell (right) and styrene in the core of the AUTMAB micelles (left). Diameters were obtained from SANS mesasurements.

temperature, the P-NIPAM network can be prepared at temperatures below the LCST avoiding a collapse of the incomplete hydrogel network during polymerization.

Upon gamma-irradiation ternary micellar solutions of AUTMAB/NIPAM/water containing up to 10 wt-% AUTMAB copolymerize and form homogeneous clear hydrogels. In Figure 6, the clear-turbid boundary of the micellar monomer solution and the composition of the hydrogels obtained after gamma-irradiation are indicated. A photograph of the clear hydrogel is also shown. The results suggest that a multiblock copolymer is obtained, in which blocks of polymerized surfmer form micellar aggregates and blocks of P-NIPAM connect the individual micelles. Due to the γ-ray polymerization, the P-NIPAM blocks are slightly cross-linked (see Figure 1).

Clear hydrogels are also obtained upon γ-ray polymerization of AUTMAB/styrene/ NIPAM/water microemulsions, if the AUTMAB and styrene contents do not exceed 5 and 0.25 wt-%, respectively.

Incorporation of AUTMAB and styrene influence the LCST of P-NIPAM hydrogels

Table 1.
Size of AUTMAB particles as determined by SANS. Particle size was calculated by means of Guinier approximation.

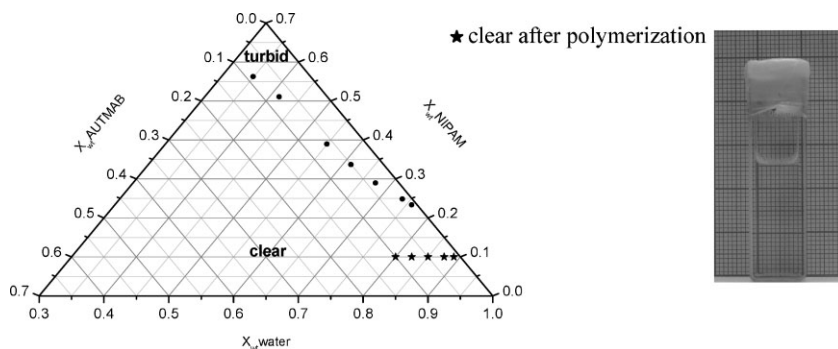| composition [wt.-%]			R [nm] at 20 °C	R [nm] at 25 °C
AUTMAB	d-styrene	NIPAM		
2.5	/	/	1.42 ± 0.02	1.65 ± 0.02
5	/	/	1.48 ± 0.02	1.64 ± 0.02
10	/	/	1.43 ± 0.03	1.49 ± 0.04
2.5	0.25	/	2.49 ± 0.01	2.33 ± 0.01
5	0.5	/	2.58 ± 0.01	2.47 ± 0.02
10	1	/	2.40 ± 0.02	2.35 ± 0.02
5	/	10	0.97 ± 0.04	0.94 ± 0.03
10	/	10	0.95 ± 0.06	0.95 ± 0.05

Figure 6.

Composition of micellar solutions for γ-ray polymerization (left) and formation of clear hydrogels (right).

(Figure 7). The LCST decreases with increasing surfactant and styrene content, while the temperature range of clouding increases upon addition of surfactant. However, variations in NIPAM concentration at constant AUTMAB concentration have only little influence on the LCST.

While the swelling of dry P-NIPAM gels in water is only moderate, the presence of AUTMAB in the gel increases the swelling up to a factor of 30 compared with the pure P-NIPAM gel (Figure 8). This can be explained by the strong osmotic pressure originating from the positive charges of the cationic surfactant copolymerized in the gel. Because of the temperature-dependence of the osmotic pressure, the

swelling increases with temperature. Above the LCST, the swelling even dominates over the volume decrease caused by the P-NIPAM part of the gel provided that more than 2.5 wt.-% AUTMAB are present in the hydrogel (Figure 9).

For AUTMAB/NIPAM hydrogels with low AUTMAB content a reversible swelling and shrinkage behaviour is observed. Figure 10 shows the reversible swelling of a hydrogel composed of 1 wt.-% AUTMAB and 10 wt-% NIPAM in Milli-Q-water. At $20\,^{\circ}C$ gels swell up to $S = 31\,g_{water}/g_{dry\ gel}$ within 8 hours, and shrink to $S = 2\,g_{water}/g_{dry\ gel}$, if the temperature is raised to $50\,^{\circ}C$.

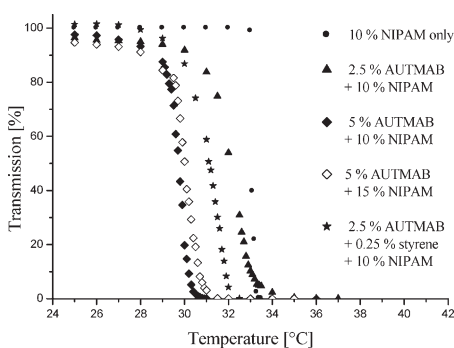The NIPAM concentration also influences the swelling of the hydrogels.

Figure 7.

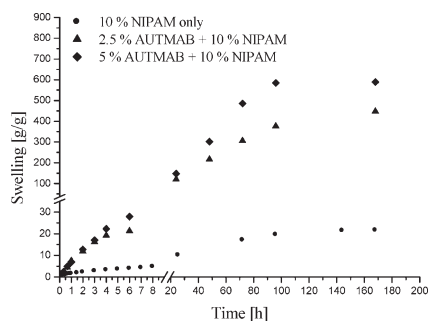Change of transparency of various NIPAM/AUTMAB hydrogels and pure P-NIPAM gel with temperature ($\lambda = 500$ nm).

Figure 8.

Swelling of AUTMAB/NIPAM and pure P-NIPAM hydrogels in water as a function of time (T = 20 °C). Swelling is defined as $(W_s - W_d)/W_d$, W_s and W_d being the weight (in g) of swollen and dried hydrogel, respectively.
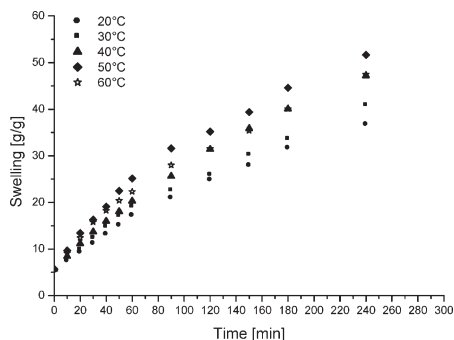
Figure 9.

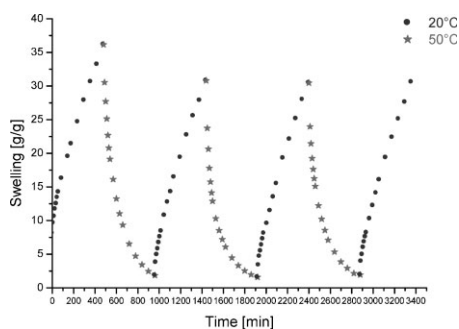Swelling of AUTMAB/NIPAM hydrogels (5 wt-% AUTMAB + 10 wt-% NIPAM) with time at different temperatures.

Figure 11.

Swelling of AUTMAB/NIPAM hydrogels containing 2.5 wt.-% AUTMAB and 10 or 15 wt.-% NIPAM at 20 °C.

Figure 10.

Reversible swelling of a hydrogel containing 1 wt.-% AUTMAB and 10 wt.-% NIPAM in water as a function of time.

Figure 12.

Mechanical behaviour under compression load for a hydrogel composed of 2.5 wt-% AUTMAB, 0.25 wt.-% styrene and 10 wt-% NIPAM (upper row) and a pure P-NIPAM hydrogel (lower row).

AUTMAB/NIPAM hydrogels with a higher NIPAM content of 15 wt.-% show a slower and lower swelling in comparison with hydrogels containing 10 wt.-% NIPAM (Figure 11).

Our studies also show that the mechanical stability of the hydrogels obtained from micellar solutions and microemulsions is considerably higher. While pure P-NIPAM hydrogels are disrupted under low compression, gels polymerized from micellar solution or microemulsion can be reversibly compressed (Figure 12).

Conclusions

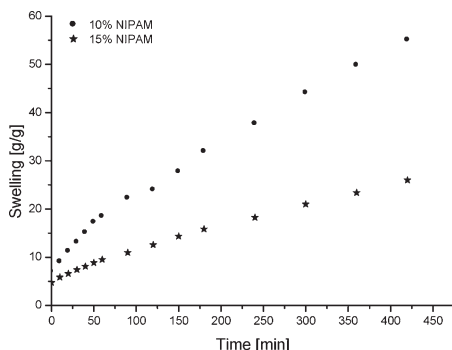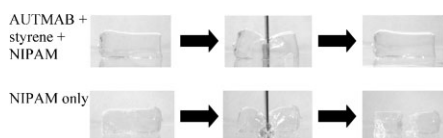Our studies show that clear, intelligent hydrogels can prepared in a one-step radiation-induced polymerization of micellar aqueous comonomer solutions and microemulsions containing cationic surfactant monomer AUTMAB and NIPAM. The polymerization method has not been reported before. Our results indicate that incorporation of surfmer in the hydrogel network and subsequent gamma-irradiation lead to a physically and chemically cross-linked gel structure with improved mechanical stability. Quantitative studies are in progress and will be published elsewhere. Due to the charged headgroups of the surfmer, a rapid and reversible swelling of the hydrogels is observed as in other surfactant containing gels[2,4]. Different from other gels[1,2], our hydrogels show a reversible clear-turbid transition at the LCST. Therefore, the hydrogels might be useful as optical switches, for example.

In further work, the copolymerization of NIPAM and non-ionic surfmers will be

studied, and pH-sensitive hydrogels based on acrylic acid and a surfmer will be prepared.

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