Photopolymerization as Alternative Concept for Synthesis of Poly(*N*-isopropylacrylamide)-Clay Nanocomposite Hydrogels

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Summary: In this work the photopolymerization of *N*-isopropylacrylamide is described as an alternative method to synthesize thermosensitive NC-gels. Tensile measurements show elongations at break up to 1000%. The mechanical properties of photopolymerized NC-gels strongly depend on the conditions during the preparation, e.g. intensity of radiation, wavelength, irradiation time. The characterization by microscopic methods (AFM, SEM, TEM) and rheology shows as a result a physical adsorption of polymerchains on the clay surface. Consequently, for the first time mechanical stable, homogeneous thermosensitive NC-gels could be obtained by mixing poly(*N*-isopropylacrylamide) solutions with an aqueous clay dispersion.

Keywords: clay; gelation; microstructure; nanocomposites; photopolymerization

Introduction

Hydrogels are cross-linked networks with an amazing potential for applications.[1–3] Due to their unique thermosensitive swelling behavior these hydrogels are integrated into microfluidic devices as pumps, valves etc.[4,5] An aim of these applications is to realize lab-on-a-chip-products allowing numerous diagnoses of diseases in a fast, simple and non-expensive way. Furthermore these hydrogels are used for tactile communication systems and sensors.[6] The currently used chemically cross-linked hydrogels are too weak and too brittle to withstand high stresses and strains. Consequently, they are unsuitable for many applications. Many scientific groups worldwide are trying to synthesize new kinds of mechanically stable hydrogels with high swelling degrees. Mainly two concepts for the preparation of such hydrogels are known: The interpenetrating networks and hydrogels cross-linked with cyclodextrines.[7,8] These preparation methods are often too complex to use these hydrogels in applications, in which high throughput manufacturing of patterned gels are of fundamental importance.

On this account Haraguchi *et al.* developed a new kind of mechanically stable hydrogels with high swelling degrees, the so-called nanocomposite hydrogels.[9,10,11] The free radical polymerization of acrylamides, e.g. poly(*N*-isopropylacrylamide), is carried out in water in the presence of Laponite. Laponite is a synthetic hectorite clay type. These inorganic particles are approx. 40 nm in diameter and are 1 nm thick.[12] Clay particles are easy to disperse in water due to their ionic structure. Their surfaces are negatively charged while the edges are positively charged (Laponite XLG). Increasing the Laponite XLG content over 2 wt.-%, a house of cards structure is formed, resulting in an increase of viscosity of the aqueous dispersion. In order to prepare NC-gels it is better to use Laponite XLS. In this case the edges are modified by pyrophosphate ions. So both, surface and edges are negatively charged and a formation of the house of cards structure is avoided.

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Haraguchi *et al.*,[11,13,14] Shibayama *et al.*, [15,16] and Miyazaki *et al.* [17,18] investigated the gelation process extensively by dynamic light scattering and small angle neutron scattering. In their works the initiation of the free radical polymerization is carried out with KPS and TEMED. The thermal initiated polymerization cannot be stopped, thus many important information regarding the gelation mechanism are lost.

Therefore we developed the photoinduced polymerization. [19,20] The photoinitiator 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) generates radicals by a homolytic Norrish type I cleavage after absorption of UV-light (360 nm).[21] Estimating the conversion of the monomer *N*-isopropylacrylamide by ^{1}H-NMR shows an immediate termination of the polymerization as soon as the UV-irradiation stops.

There are four benefits using the photopolymerization: (i) The immediate termination of the photopolymerization allows an intensive characterization of the gelation mechanism in the different states of the gelation process, (ii) the photopolymerization gives more information about the physical interactions between the polymer and the clay surface, (iii) the photopolymerization allows a defined patterning on the micrometer scale of NC-gels for microfluidic and sensoric applications by lithographic methods (publication in preparation), and (iv) the investigation of the gelation process of photopolymerized NC-gels leads to alternative preparation methods of NC-gels by mixing polymer and clay solutions.

Experimental Part

Samples

N-Isopropylacrylamide (NIPAAm, Acros Co.) was purified by recrystallization from n-hexane, followed by drying under vacuum. The inorganic clay, a synthetic hectorite called "Laponite XLS" (92.32 wt % $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$ + 7.68 wt % $Na_4P_2O_7$) from Rockwood Specialties Inc. was used after washing and freeze-drying. The photoinitiator 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959, Aldrich) was used as received. The solution was purged for more than 1 h with argon to remove any oxygen. Throughout all experiments, oxygen was excluded from the reaction system. To receive hydrogels by photopolymerization, a transparent aqueous solution consisting of water, inorganic clay (Laponite XLS), NIPAAm, and photoinitiator was prepared. The concentrations of NIPAAm and photoinitiator (PI) were kept constant with 10 wt % monomer and 0.3 wt % PI, respectively. The amount of clay was varied over a wide range between 3 and 15 mol % in the aqueous solution. The sample codes were defined by the concentration of clay in water. ("NC2" is equal to a 2 mol % aqueous clay suspension). The photopolymerization was carried out in an argon atmosphere through UV irradiation. ($\lambda > 360$ nm, mercury UV lamp of 900 W, (LOT Oriel), approximately 5 mW/cm^2 at $\lambda = 360$ nm) at an exposure time of 120 s. A UV-filter was used to prevent degradation of the polymer chains caused by short wavelengths below 200 nm. The used UV bandpass filter (Schott UG11) also adsorbed visible light to prevent an increase of the temperature of the reaction above the LCST of PNIPAAm. Additionally, the samples were placed in ice-bath to keep a constant temperature. To avoid inhomogeneities in the structure of hydrogels caused by UV irradiation, NMR tubes (with an outer diameter of 5.0 mm) were used for the photopolymerization. Using a wavelength of 360 nm (which is not the absorption peak of the photoinitiator) and very thin NMR tubes, we observed no perceptible intensity gradient of the radiation across the sample tubes. Furthermore, during UV exposure we rotated the tubes in order to preclude a surface reaction. It was shown that UV light with a wavelength of 360 nm will almost not be absorbed by the NMR tubes.

Tensile Mechanical Properties

Tensile measurements were performed on as-prepared photopolymerized NC-gels (size: 5 mm diameter x 50 mm lengths)

using a Zwick/Roell apparatus under the following conditions: temperature, 25 °C; crosshead speed, 50 mm min^{-1}. The intial cross section (23 mm^2) was used to calculate the tensile strengths.

Atomic Force Microscopy

The NC-hydrogel tubes were cooled with liquid nitrogen. Afterwards the samples were cut into thin films (approx. 100 nm) and examined with a NanoWizard 2 (JPK). Silicon nitride Cantilever PPP-CONTR-50 and PPP-NCHR-50 (NANOSENSORS) were used.

Scanning Electron Microscopy

SEM images were performed on freeze dried and air-dried NC-gels with HITACHI S-5000 at 30 kV.

Transmission Electron Microscopy

TEM characterization was realized using a Philips EM410 at 80 kV.

Results and Discussion

The photopolymerization of the system (NIPAAm/Laponite XLS/Irgacure 2959) producing bulk hydrogels was described for the first time by Ferse *et al.* [19,20] The resulting gels showed thermosensitive behavior and improved mechanical properties. Photopolymerization is a suitable technique to investigate the gelation process during a free radical polymerization. ^{1}H-NMR measurements showed that the conversion stopped immediately after interrupting the UV exposure, thus making it possible to observe the gelation process at different polymerization stages separately. A continuous transition from sol to gel could be observed with DLS on irradiated samples with 5 mW/cm^2. With additional static light scattering measurements, the mechanism of the gelation process was clarified: The formed PNIPAAm chains closely attach to the surface in the early stages of polymerization. The strong physical interactions between the clay surface and the polymer chains lead to a compact polymer layer surrounding the clay sheets. As a result, it is not possible to destroy the physical interactions between PNIPAAm and clay, the NC gel does not dissolve. [20]

Haraguchi *et al.* studied the mechanical properties of photopolymerized NC-gels.[22] But he did not give specifications of the performed synthesis. We could show that the mechanical properties and swelling behavior strongly depend on the conditions during preparation. It is essential to use a cut-off filter absorbing all light of wavelenghts below 350 nm. Hence no yellowish coloring occurs, which is an indication for a polymer degradation. Furthermore the power of irradiation plays a decisive role to obtain homogeneous hydrogels with excellent properties. The photopolymerization of homogeneous NC-gels should be realized applying a maximum power of 5 mW/cm^2. The irradiation time has to be chosen as short as possible to avoid an overexposure resulting in brittle gel samples. Irradiation times of more than 130 s result in mechanically unstable NC-gels.

Figure 1 shows the stress-strain curves.

The elongations at break of the photopolymerized NC-gels (NC5: 1152%) have slightly higher values than thermal initiated NC-gels (NC5: ~1035% [10]). Certainly the tensile strength of these photopolymerized NC-gels is smaller than the one of thermal initiated gels.[10] That means the described experimental procedure leads to photopolymerized NC-gels with better elongation

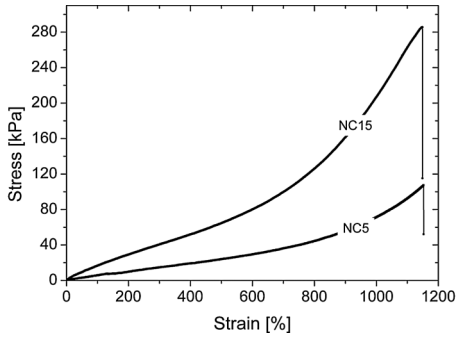

Figure 1.
Stress-strain curves of photopolymerized NC-gels with different clay contents.

values compared to the usually synthesized NC-gels whereas the low tensile strength of photopolymerized NC-gels leads to softer hydrogels.

A gelation of NC-gels occurs due to the strong physical interactions between the PNIPAAm chains and the clay surface. Polymer chains adsorb on the clay surface by hydrogen bonding, surrounding the inorganic particles with a compact polymer layer. Consequently, clay sheets cross-link PNIPAAm chains to a network. Clay acts as multi-functional crosslinker.

Using microscopic techniques, the distribution of clay particles in the gel can be characterized. The photopolymerized NC-gels have a porous structure, which can be observed in SEM experiments very well. Figure 2 shows the porous nature of a photopolymerized and freeze-dried NC-gel obtained by SEM.

SEM studies on air-dried samples show the same results concerning the porosity of gels (Figure 3). Sections holding a high amount of polymer alternate with areas of a low polymer concentration. Single clay particles embedded in a polymer matrix can be observed. These particles do not posses an uniform size and shape. The reason for the formation of the porous structure of photopolymerized NC-gels is not known yet. It is possible that the preparation conditions for the photopolymerization are reponsible for porous structure. Usual thermal intitiated NC-gele show no porous behavior.

Figure 4 shows the corresponding TEM-images of the same samples. The clay particles can be seen as dark dots.

Figure 5 shows a photopolymerized NC6-gel characterized by AFM. In the polymer matrix (light areas) a random distribution of clay particles (bright dots) can be detected whereas the pores (dark areas) are sections without polymer. Only the clay sheets on the surface, causing an elevation of the hydrogel surface, could be detected. They appear in bright dots in the AFM-images.

Assuming an uniform distribution of the particles in the hydrogel the AFM-measurements allow to estimate an average distance of clay sheets in the photopolymerized NC-gels. Three preconditions are made to determine the average distance: (i) The particles are described as point masses, (ii) the distance between two clay particles should not exceed 100 nm, and (iii) the distance line between two particles should not be intersected by a third one. The results show a logarithmic distribution of the clay platelets in the gel:

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{\ln(x)-y}{\sigma}\right)^2} \cdot \frac{1}{x} \qquad (1)$$

The average distance of clay sheets at different clay concentrations of the photo-

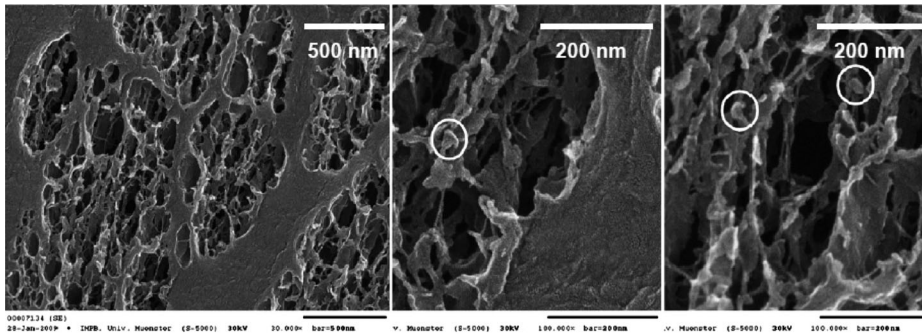

Figure 2.
SEM results of a photopolymerized NC6 sample, the white circles emphasize small clay sheets attached to the polymer matrix.

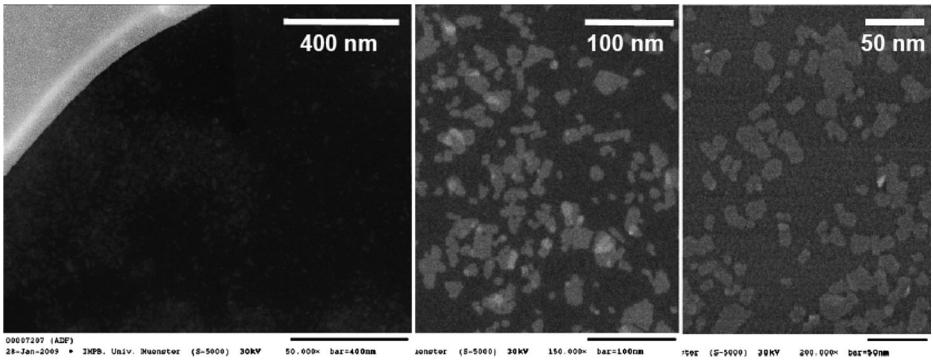

Figure 3.
SEM images of a photopolymerized air-dried NC6 sample.

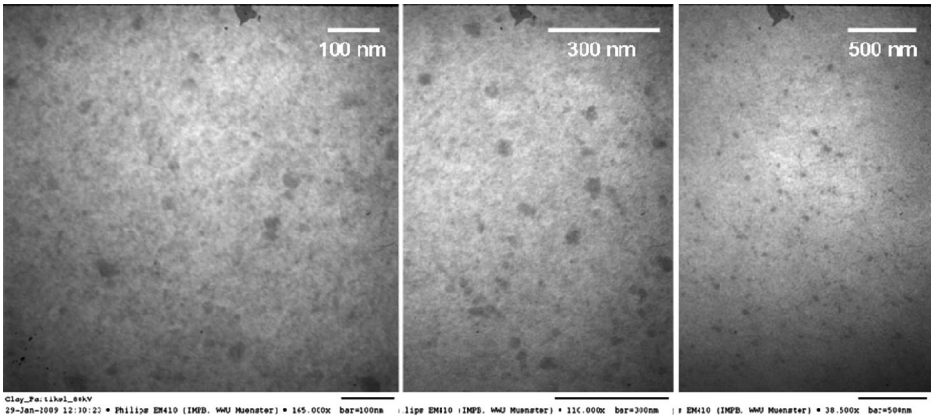

Figure 4.
TEM-Images of a photopolymerized NC6 smple.

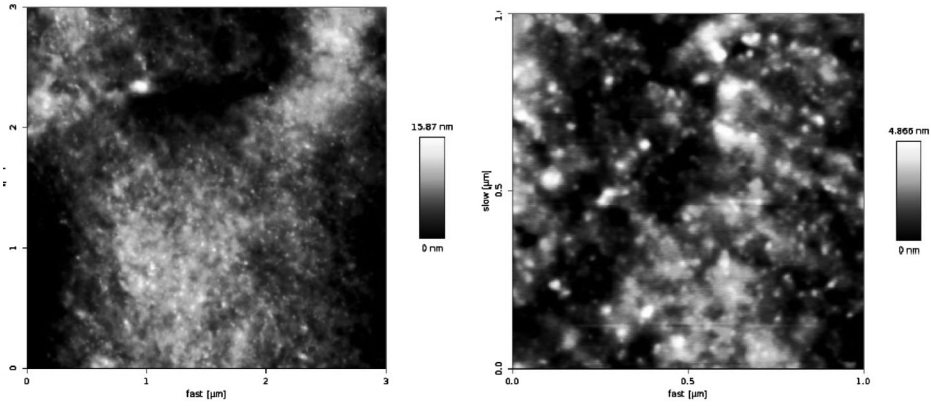

Figure 5.
AFM-images of a photopolymerized swollen NC6-gel; left figure: scan area $3 \times 3\ \mu m^2$, z-range:15 µm; right figure: scan area $1 \times 1\ \mu m^2$, z-range 1.5 µm; The bright dots are the clay particles on the hydrogel surface, dark areas are pores of the gel.

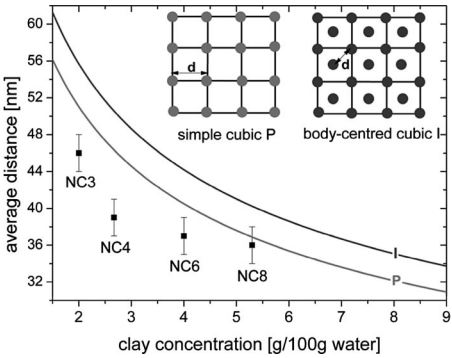

Figure 6.
Average distance between two clay particles in photo-polymerized NC-gels.

polymerized NC-gels is shown in Figure 6. The distance between the particles decreases with increasing clay content. At higher clay concentration the distances reach a constant value of approx. 35 nm. This is due to the fact that the approach is limited by the size of the clay sheets with an average diameter of approx. 40 nm. The calculation of the average distance of clay for a simple cubic structure (P) or a body-centred cubic structure (I) verifies the results.

The effective functionality of the cross-linker clay determined by the rubber elasticity theory gives information about the adsorption of the polymer chains on the clay surface. Nie and Oppermann [23] published the values of the effective functionality of typically thermal initiated NC-gels. These values decrease with an increase of the clay content. Typically the polymerization is carried out with KPS molecules, which dissociate in water into ions and adsorb on the clay surface by ionic interactions. Consequently the polymerization starts from the clay surface and polymer brushes are already formed in the early stage of polymerization.[11] The ends of the polymer chains are ionically fixed to the clay surface. Each KPS molecule on the clay surface represents one junction. Increasing the clay concentration of the initial reaction solution, the KPS molecules are distributed to more clay particles and the effective functionality decreases.

In contrast the photoinitiator does not posses the essential ionic properties to interact with the clay surface. The polymerization starts in the solution and only in a second step the polymer chains adsorb on the clay surface by H-bonds. A polymer layer surrounds the clay particles. If the concentration of clay is low, all polymer chains form a compact layer and only a few free polymer chains cross-link other clay platelets. Increasing the clay content in the reaction solution, the polymer chains are distributed to more particles. Consequently, the thickness of the polymerlayer decreases. The layer gets brittle and more free polymer chains cross-link other clay particles. Thus the functionality increases alongside the clay content. [24] These results show that no ionic interactions are necessary to obtain NC-hydrogels. The cross-linking process is caused by a physical adsorption of polymer chains on the clay surface. The formation of H-bonds for example leads to a permanent adsorption. Therefore it should even be possible to obtain NC-gels by simply mixing polymer and clay solutions.

Without any chemical reaction, a simple additive free mixing process of linear PNIPAAm and clay solutions leads to homogenous hydrogels. The obtained NC-gels show a good mechanical stability and transparency. This preparation method of mechanically stable, homogeneous, transparent thermosensitve NC-gels is described for the first time. Other attempts to synthesize thermosensitive mix-gels as already described by Haraguchi et al. [11] lead only to turbid and brittle hydrogel samples.

Under stirring, a clay suspension is added to the aqueous polymer solution. Heating this pre-gel solution above the phase transition temperature of PNIPAAm, a macroscopic gelation can be obtained. A PNIPAAm mix-gel is shown in Figure 7.

Varying molar mass and concentration of polymer and clay strongly influences the

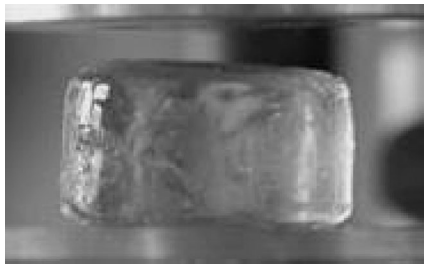

Figure 7.
Example of a thermosensitive nanocomoposite mix-gel.

gel's properties. To characterize the mechanical properties of mix-gels, further investigations will be performed. A more detailed discussion of the gelation mechanism and the mechanical properties is in preparation.

Conclusion

The photopolymerization is a suitable technique to prepare NC-gels with excellent mechanical properties. Tensile measurements show elongations at break of about 1000%. The mechanical properties and swelling ratios are comparable to results obtained by typical, thermal initiated synthesized NC-gels. Applying lithographic methods, the photopolymerization can be used to pattern well defined NC-gel structures in a micrometer scale. For later applications, e.g. microfluidic devices, an easy patterning procedure of mechanically stable hydrogels is an essential point of interest. Furthermore, the method allows an intensive characterization of the gelation mechanism in the different states of polymerization due to a possible termination of the free radical polymerization by interrupting the UV irradiation. The most fundamental result of a detailed characterization of the initiation shows a physical adsorption of PNIPAAm chains on the clay surface. Consequently, no ionic interactions are necessary. This result leads to alternative preparation methods of homogeneous, mechanically stable, thermosensitive NC-gels by mixing PNIPAAm- and clay solutions without any chemical reactions. The cross-linking process is caused by a physical adsorption of polymer chains on the clay surface. An easy adjustment of mechanical properties and swelling behavior can be performed by a variation of the molar mass and the concentration of polymer and clay.

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