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Temperature and pH Sensitive Polymers in Water – From Solution to Thin Films

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SUMMARY: A series of temperature and pH sensitive polymers which contain both temperature and pH sensitive components were synthesised by copolymerization of N-isopropylacrylamide (NIPAAm) and acrylamide derivatives containing a spacer and a sensitive headgroup. The cloud point and heat of transition (ΔH_{PT}) of aqueous solutions of polymers with various compositions were measured by means of DSC. The observed cloud points and ΔH_{PT} values strongly depend on the polymer composition and the pH value. The irradiation of dimethylmaleinimide groups (DMIAAm) bearing copolymers with UV light resulted in crosslinking of the polymers. The prepared thin layers showed fast temperature dependent swelling with transition temperatures similar to the uncrosslinked polymers.

Introduction

The effect of the lower critical solution temperature (LCST) in solutions of linear macromolecules and in polymer gels is increasingly of interest to numerous academic and industrial laboratories. These polymers undergo a discontinuous or continuous phase transition in response to temperature, pH-value, solvent composition, etc.[1, 2] The characteristics of these polymeric materials have been studied extensively as starting materials for drug delivery systems, in separation systems, etc.[3, 4] The application of these materials in chemomechanical actuators has also been proposed.[5]

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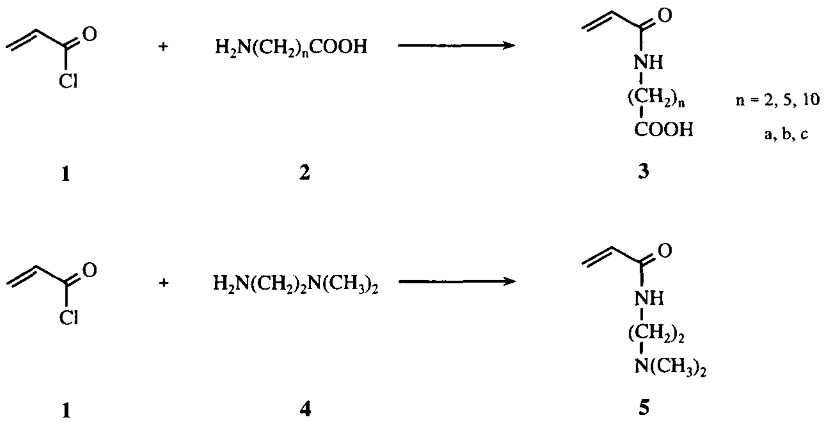
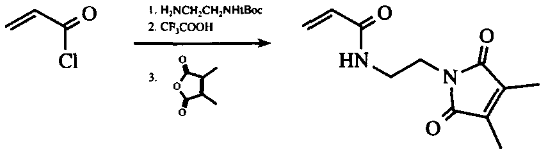
One of the most intensively studied polymers in this field is poly(N-isopropylacrylamide) (PNIPAAm) which exhibits a sharp phase transition in water at 32 °C.[2] The reason for this sharp phase transition is a good balance between hydrophilic and hydrophobic interactions in the polymer. Raising the temperature of an aqueous PNIPAAm solution above the LCST causes a coil-to-globule transition, followed by a phase separation. The LCST of PNIPAAm copolymers is strongly influenced by the nature of the comonomer. Hydrophobic compounds lower the LCST and hydrophilic compounds raise it.[6, 7] Owing to the fact that the solution behaviour of linear polymers can be correlated with the swelling properties of there gels, the preparation and investigation of soluble polymers is a promissing field for the development of new actuator materials with adjustable switching points.

Sensitive soluble polymers

In order to develope materials for this purpose temperature and pH sensitive polymers were prepared by copolymerization of N-isopropylacrylamide (NIPAAm) with differing amounts of acrylamide derivatives.[8], [9] The derivatives contained spacer groups with different chain lengths and a sensitive head group. Homo- and copolymerization of NIPAAm with the comonomers **3a** – **3c**, **5** and **6** (Scheme 1) was carried out in dioxane using 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator at 70 °C for 7 h with a total monomer concentration of 0.55 mol/L.





1 **6**

Scheme 1: Synthesis of the functional monomers (**3** = C_nAAm, **5** = C_2NAAm, **6** = DMIAAm)

The phase transition of a temperature sensitive polymer at the critical temperature is a multi-step process. For PNIPAAm it is well investigated.[10] In an aqueous solution of this polymer there exists a well-balanced equilibrium between hydrophilic interactions (hydrogen bonds between the polymer and the water molecules) and hydrophobic interactions (van-der-Waals interactions in the polymer). Below the LCST the hydrophilic interactions dominate and the polymer is soluble. However, above the LCST the hydrophobic interactions become dominant. If the concentration is high enough the polymer precipitates from solution. The phase transition is accompanied by a release of bound water from the polymer chain. This is an endothermic process and the heat of reaction could be determinated by DSC.[11] In the literature also other methods, like light scattering (detection of the coil-to-globule transition of the polymer chain),[10] turbidimetry (detection of the phase separation)[12] or determination of *the degree of swelling,*[1] *were used for the determination of the phase transition temperatures.* With a constant heating rate, usual for such experiments, the measured cloud point depends on the method that was used. The measured temperatures from light scattering and turbidimetric experiments were even higher than those from DSC, although the results depend upon the heating rate and the concentration of the aqueous solution.[13] For semi-dilute solutions the heat of demixing as well as the LCST are independent of the concentration and the molecular mass of the polymer.[2, 14, 15]

In our experiments we chose DSC as a standard method to determine the LCST. DSC allowed us to measure the phase transition over a wide range of temperatures and pH values. The DSC curves were obtained from a 5 wt.-% polymer solution. The onset of the thermogram corresponds to the temperature of collapse.[16] Fig. 1 shows the cloud points of the PNIPAAm homo- and copolymers in water.

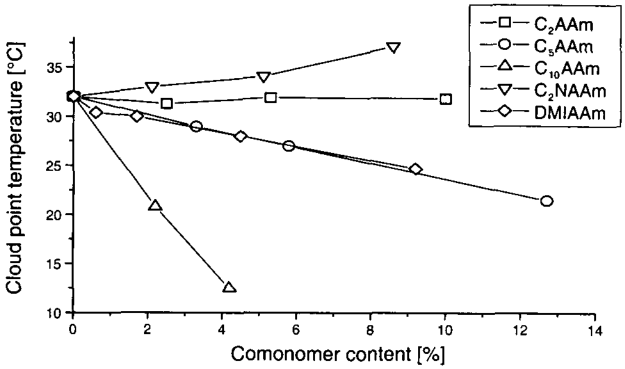


Fig. 1: Cloud point temperatures of several PNIPAAm copolymer/water solutions

Aqueous solutions of the copolymers showed lower critical solution temperature behaviour, which was dependent on the comonomer content. The cloud points of the aqueous solutions of the acidic copolymers decreased with increasing comonomer content and spacer chain length. For the short comonomer C_2AAm the change in the hydrophobicity is rather small leading to no significant change in the cloud points and they were nearly independent of the polymer composition. With a long alkyl chain in the comonomer the hydrophobicity of the spacer dominated over the hydrophilicity of the carboxylic group. The copolymer becomes more hydrophobic and the cloud points decreased.[8]

The cloud points of aqueous C_2NAAm copolymer solutions increased with increasing comonomer content. As it can be estimated from the pK values of low molecular weight analogous the degree of ionization in water of the functional groups for C_2NAAm copolymers is twice as high as for the C_2AAm copolymers. The higher degree of ionization increases the hydrophilicity of the polymer and hence the cloud points were increased.

The cloud points were also strongly dependent on the pH-value of the solution (Fig. 2). An increase of the pH value led to a significant increase in the cloud points due to a change to a more hydrophilic copolymer. The cloud points increased greatly between pH 6 and pH 7 for all polymers except pure homopolymer PNIPAAm which displayed no sensitivity to pH. At low pH all carboxylic groups were protonated and the polymers were more hydrophobic resulting in lower cloud points. Raising the pH over the critical value of pH 6 the acidic comonomer units were ionized. The polymer was more hydrophilic and the cloud point increased. For the basic copolymers the pH behaviour is reversed. As can be seen from the last two figures it is possible to adjust the cloud points over a wide range of temperatures by changing the polymer composition and/or the pH of the solution.

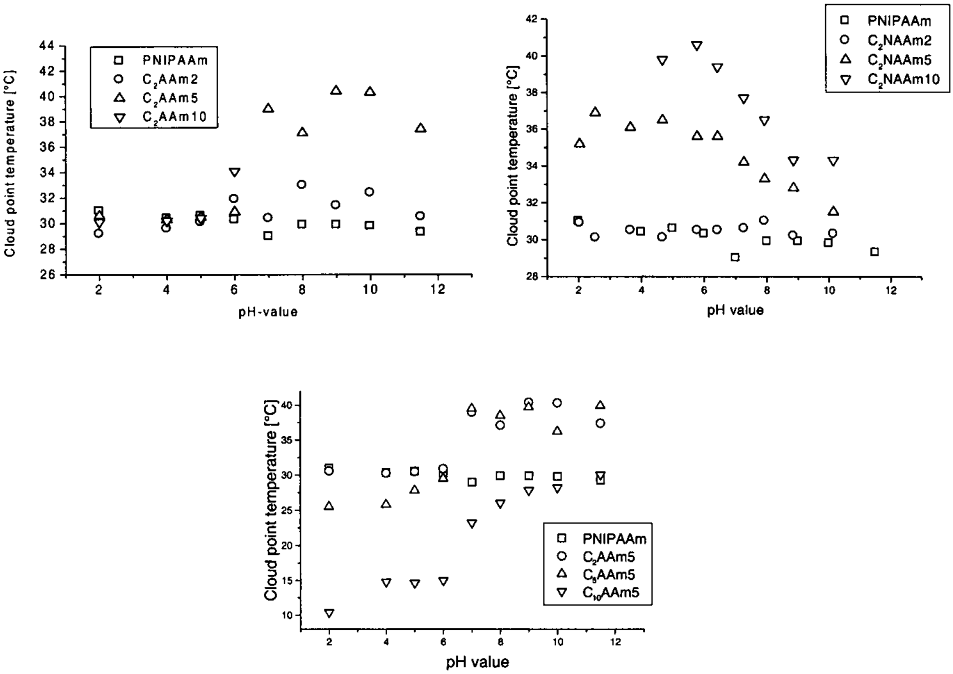


Fig. 2: Dependence of the cloud point temperaures of aqueous PNIPAAm copolymer solutions on the pH value

In Fig. 3 the temperature and heat of phase transition (ΔH_{PT}) in water are shown. Additionally to the discussed copolymers the LCST/ΔH_{PT} values of C_2NAAm copolymers ionically modified with methane sulfonic acid (MS) and butane sulfonic acid (BS) are shown. The ΔH_{PT} values decreased with increased cloud point values. With modification of PNIPAAm to a more hydrophilic polymer the cloud point increased and the heat of transition decreased. This can also be seen by the change of the cloud points of PNIPAAm copolymers by changing the pH value. E. g. for C_nAAm copolymers, at low pH values the polymers are not ionized and the cloud points and ΔH_{PT} values are in the range of those in water, at high pH values the polymers are in an ionized state, which resulted in an increase of the cloud points (Fig. 2 a and c) and a decrease of ΔH_{PT}.

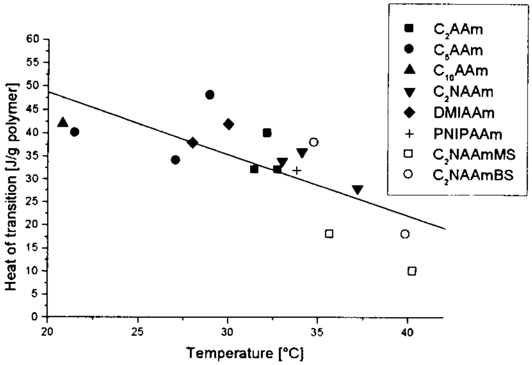


Fig. 3: Heat of phase transition of PNIPAAm copolymer/water solutions

It has been suggested that LCST behaviour is caused by a critical hydrophobic/hydrophilic ballance of polymer side groups. At low temperatures, the strong hydrogen bonding between hydrophilic groups and water leads to a good solubility of the polymer in water. Besides the hydrogen bonds between polar groups and water molecules, where they can retain their ordered structure, the water molecules must reorient around the nonpolar region of solutes, being unable to hydrogen bond with them, resulting in a decreased entropy upon mixing (negative ΔS_{mix}). By raising the temperature above the cloud point, the entropy term dominates the otherwise exothermic enthalpy (ΔH_{mix}) of the formed hydrogen bonds. The free energy change upon mixing ($\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$) becomes positive, with the consequence of phase separation.[2]

Hence, the heat of phase transition of an aqueous PNIPAAm solution is mainly related to the destructuring of water around the hydrophobic N-isopropyl groups. An increase in hydrophilicity of the polymer leads to a decrease of the amount of destructured water.[16] However, ΔH_{mix} decreases and, moreover, ΔS_{mix} decreases greatly resulting in an increase of the cloud points. Thus the cloud points are influenced by both the amount of comonomer and its hydrophilicity.

The PNIPAAm-copolymer/water solutions underwent a phase separation during heating. For the homo-PNIPAAm/water system the mechanism of phase separation has been well investigated.5) During heating of a semi-dilute solution due to the destruction of hydrogen bonds and increasing hydrophobic interactions the PNIPAAm chains first associate, then collapse and a phase separation occurs. For the viscosity of a polymer solution this means an association of molecules leads to an increase in the viscosity due to the formation of bigger particles. In a second step the polymer chains collapse. As known from the FLORY-FOX-theory[17] the solution viscosity of polymer particles depends upon their hydrodynamic radius. During the coil-to-globule transition of the polymer chain the hydrodynamic radius decreases. As a result the viscosity also decreases. Comparison of these results with those from viscosimetric measurements showed a two step mechanism for the phase separation.

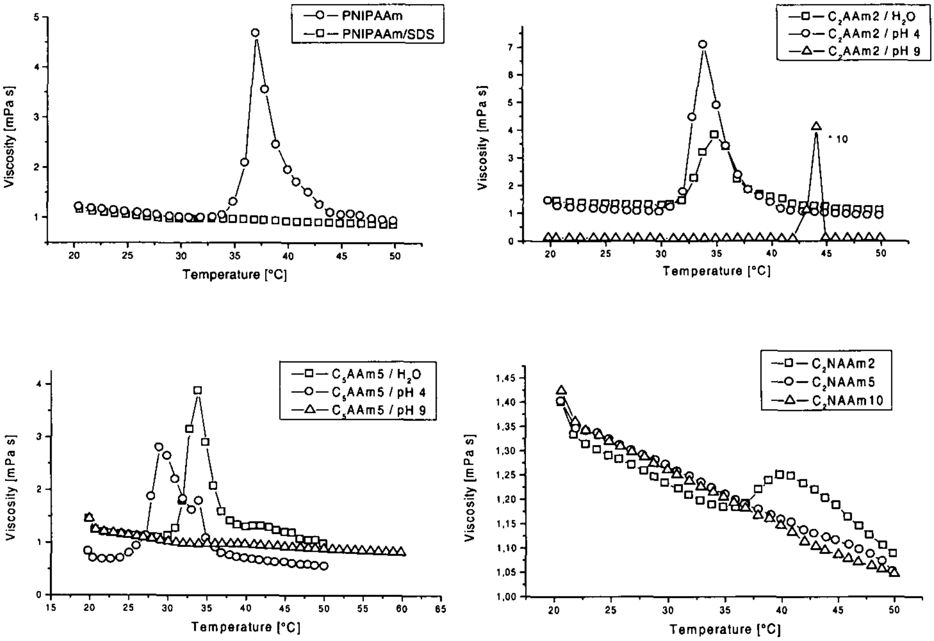


Fig. 4: Effect of temperature on the dynamic viscosity of various aqueous polymer solutions

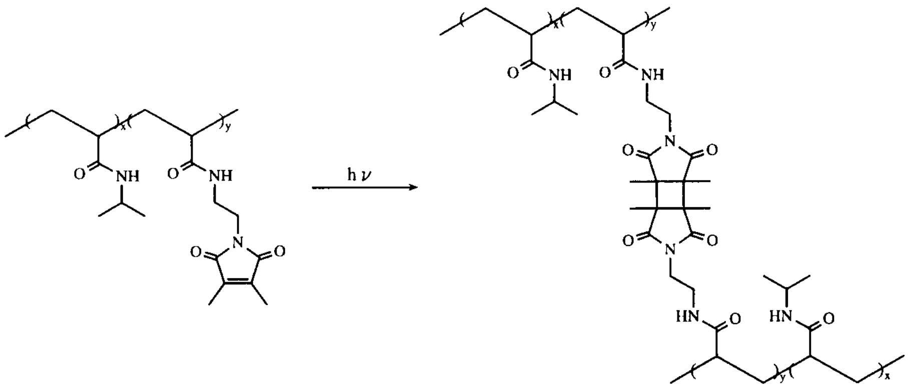
Fig. 4 shows the dynamic viscosities η of the several copolymers in water and at different pH values. At temperatures below the cloud point the viscosities are in the range of diluted polymer solutions and slightly decreases with temperature. If the cloud points were passed in pure water and at low pH a strong increase of the viscosity could be observed. At this point the polymer chains start to aggregate forming bigger particles. As a result the viscosity increases. In a second step which is a bit slower the polymer chains collapse and the particle size decreases. For this reason the viscosity also decreases. At high pH or by addition of a surfactant no aggregation could be observed. The negatively charged groups of the comonomer or of the absorped surfactant prevent the polymer chains from aggregation due to their electrostatic repulsion.

Sensitive polymer gels

The characteristics of the soluble polymers can be compared with those of gels. The gels behaved similarly to their soluble analogous. Additionally they showed temperature and pH depended swelling. Due to the fact that swelling/deswelling is a diffusion controlled process, the macroscopic size of the gel is important for the kinetic of swelling. The rate of swelling is inversely proportional to the square of the characterisitic length of the gel. To improve the response time to a usable level it is necessary to reduce the gel size dramatically. We aim to use these materials in microsystems (e. g. microactuators) in which the gel sizes are reduced to the µm-range.[18, 19]

The route we chose to synthesize thin films of sensitive polymers on Si-wafers as supporting material involved the photocrosslinking of linear prepolymers. This method is advantageous for two reasons: Thin films can easily be prepared and networks can be formed from polymers with well defined structures.

The procedure for the preparation of thin films on Si-wafers was as follows: The wafer was coated with a prepolymer solution. After evaporation the dry film was subsequently crosslinked via UV-irradiation. For this reason a special NIPAAm copolymer was synthezised by radical copolymerization of NIPAAm with dimethylmaleinimide (DMI) bearing acrylamide groups (monomer **6**).[9] The DMI-chromophore reacts via a [2+2]-cycloaddition under irradiation. This can be used to crosslink the polymer (Scheme 2).[20]



Scheme 2: Photo crosslinking reaction

The chromophore influenced the phase transition temperature. An increasing amount of chromophore caused a decrease of the phase transition temperature. The crosslinking by UV-irradiation formed water swellable films with LCST behaviour. This could be seen from the temperature dependence of the degree of swelling and from DSC measurements. The cloud point/LCST values of the prepolymers and the networks are summarized in Tab. 1.

Tab. 1: Phase transition temperatures of sensitive photopolymers

copolymer composition (content of **6**)	linear prepolymer	crosslinked polymer	
	cloud point $_{\mathrm{DSC}}$	$\mathrm{LCST}_{\mathrm{DSC}}$	$\mathrm{LCST}_{\mathrm{swell}}$
0.6 %	30.4 °C	-	-
1.7 %	30.0 °C	28.8 °C	32 °C
4.5 %	28.0 °C	27.0 °C	26 °C
9.2 %	24.7 °C	21.6 °C	20 °C

The change in film thickness due to swelling depended on the crosslinking density. For a very weakly crosslinked network a value of $d_{\mathrm{swollen}}/d_{\mathrm{dry}} = 10$ (d = film thickness) was typical. The comonomer content of 0.6 % for **6** was not enough to form a stable network.

Conclusions

The LCST analysis of soluble sensitive prepolymers is an easy way to demonstrate the potential which can be expected from gels in mm- and µm-ranges. Using the described prepolymers it is possible to generate and pattern temperature sensitive polymer films for use as microactuators. Furthermore, the synthetic route offers the possibility to modify the prepolymer by copolymerization. The aim of modification is the synthesis of polymers which can convert changes not only in temperature and/or pH-value but also electric fields, solution compositions etc. or signals of molecular recognition into microactuatoric responses.

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