Cononsolvency of mono- and di-alkyl *N*-substituted poly(acrylamide)s and poly(vinyl caprolactam)

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A B S T R A C T

In this comparative study we investigate the influence of the side chain substitution pattern on the volume phase transition temperature (VPTT) of thermo-sensitive polymer microgels. We especially focus on cononsolvency of water and methanol. We compare literature data for poly(*N*-isopropylacrylamide) (PNIPAM) that shows cononsolvency to experimental data for secondary amide poly(*N*-n-propylacrylamide) (PNNPAM) as well as tertiary poly(*N,N*-diethylacrylamide) (PDEAAM) and poly(*N*-vinyl-caprolactam) (PVCL). As methods we apply size determination by dynamic light scattering (DLS) as well as differential scanning calorimetry(DSC) and theoretical calculations using COSMO-RS (conductor-like screening model for real solvents). Clear differences are found for PDEAAM and PVCL in comparison to PNIPAM and PNNPAM. We ascribe the significant differences between PNIPAM and PNNPAM on the one hand and PDEAAM and PVCL on the other hand to the amide proton, which is present in PNIPAM and PNNPAM but not in the other two polymers.

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1. Introduction

A number of thermoresponsive polymers containing amide side chains that become water insoluble above a certain temperature additionally show cononsolvency behaviour. That means that they also precipitate upon addition of a good solvent to a solution, while others do not. The aim of this study is to investigate whether the substitution pattern of the amide function decides if the polymer shows cononsolvency or not.

Thermoresponsive precipitation and re-dissolution is known for a series of polymers that contain amide side chains [1]. The most prominent representative in this group is poly(*N*-iso-propylacrylamide) (PNIPAM). It is water-soluble below a so-called lower critical solution temperature (LCST) of about 32 °C, independently of the molecular weight; at temperatures above the LCST it is water-insoluble [2]. Similar behaviour can be found for other acrylamides like poly(*N,N*-diethylacrylamide) (PDEAAM) and

polymethacrylamides like poly(*N*-isopropylmethacrylamide) [3]. However, amide side chains are no general prerequisite for this phenomenon; there are also examples with ester/ether side chains [4].

The transition can easily be observed by an increase of turbidity (at the so-called cloud point) that is caused by precipitation and forming of aggregates [5]. These aggregates can cause problems especially in scattering studies. In order to avoid such aggregates one can use high dilution or specially modified polymers [6]. Another way is addition of a crosslinker during synthesis, which leads to chemically cross-linked gels that do not precipitate but undergo pronounced shrinking when the LCST is reached [7]. Since no phase separation occurs, the transition is coined volume phase transition (VPT) and instead of LCST the term VPT temperature (VPTT) is used. To overcome the disadvantage of a broad transition because of the complexity of hydrogels, mostly colloidally stable microgels with hydrodynamic radii in the range of some tens of nanometres to a few micrometres are studied [8,9].

Some of the above mentioned thermoresponsive polymers, among them, most prominently, PNIPAM [10–12], also show so-called cononsolvency. Generally, cononsolvency describes the

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phenomenon that a polymer is soluble in two pure solvents but not in mixtures of both [11]. In the case of thermoresponsive polymers it can also be described by a decrease of the VPTT or LCST, respectively, upon addition of a cosolvent to an aqueous solution to a minimum value at a certain solvent mixing ratio. At cosolvent concentrations above that certain mixing ratio, the VPTT increases again and finally vanishes as the cosolvent is a good solvent without LCST behaviour [8,11]. This means that cononsolvency is only observed below the LCST of the polymer in water; above the LCST there is simply a transition from insoluble to soluble upon cosolvent addition.

In recent years, different polymers [13,14] have been studied concerning cononsolvency by a variety of methods in different binary solvent systems [15–17]; the most popular are combinations of water and alcohols [8,18], often methanol [11,19,20]. Like for the LCST behaviour, studies have been performed on linear polymers [11,21], cross-linked gels [10,22]. and microgels [8,23]. A schematic depiction of the cononsolvency effect of a PNIPAM microgel particle is given in Fig. 1 by showing the case at 10 °C.

A number of different methods have been established to follow and investigate the volume phase transition. Although the cloud point is an easy measure to determine the VPTT [5], there are some severe drawbacks. The change of transmittance which occurs when the turbidity of the sample changes may take place at a different temperature than the dehydration of the polymer chains [2,24]. Thus, the cloud point can deviate from the characteristic temperature determined by more advanced methods that detect quantities more directly related to the transition. Thus the cloud point cannot generally be regarded as VPTT.

One method for a more direct detection of the transition is differential scanning calorimetry (DSC). DSC detects energetic changes in the sample, that most probably result from the breaking of hydrogen bonds that lead to the collapse of a microgel or precipitation of linear polymers [25,26]. DSC shows that the transition of PNIPAM and also PDEAAM from swollen to collapsed state in water is endothermic and thus controlled by entropy [25,27,28]. From DSC measurements the peak temperature is usually considered as phase transition temperature.

In contrast to the cloud point, DSC makes it possible to observe the entire process of phase transition and not only the beginning. Hence, it is possible to determine the width of transition as difference between onset and end point of the peak [29]. Previous DSC studies showed that for PDEAAM in water the phase transition is broader and the transition entropy is lower than for PNIPAM in water [27,28]. Addition of methanol increases the peak width in case of PNIPAM but not for PDEAAM [30]. This is remarkable since it is known that PDEAAM, in contrast to PNIPAM [31], shows (almost) no cononsolvency [31]. A peculiar effect that the DSC results show is that the transition heat decreases with increasing x_{MeOH} for PNIPAM and PDEAAM. This finally leads to the case that above $x_{MeOH} = 0.2$ there is no transition detectable by DSC [30]. DSC on linear poly(N-vinylcaprolactam) (PVCL), a thermoresponsive polymer with a tertiary amide side chain and an LCST of approx. 32 °C

showed no cononsolvency [32–34] but an increase in LCST at methanol fractions above 35 vol % [35].

Scattering methods constitute a powerful tool to study the collapse of especially stimuli-responsive microgels. They can yield the particle size [8], network density [36] and behaviour of chains in the network [37,38]. Dynamic light scattering (DLS) determines the average diffusion constant D that is in inverse proportion to the hydrodynamic radius R_h. Thus, via temperature-dependent DLS it is possible to detect the change in hydrodynamic radius R_h and thus the swelling state of a microgel fast and directly. From that data, the temperature at which the inflexion point of $R_h(T)$ is found is taken as VPTT.

With DLS it is possible to detect if the phase transition is sharp or continuous. For example, in the case of PNIPAM in water a sharp transition is detected while for PDEAAM in water a more continuous phase transition is found [39]. The sharp phase transition of PNIPAM in water can be explained by the cooperative formation of intra-molecular H-bonds if temperature is increased above the VPTT [40]. As PDEAAM cannot form intramolecular H-Bonds (conf. Fig. 2) no cooperativity will occur [40], which leads to a continuous phase transition. This is in agreement with the broad peak width of PDEAAM in water found with DSC. Thus, the information one can get from the shape of $R_h(T)$ is helpful to reveal the cooperative behaviour of the polymer network during the phase transition.

Due to the cononsolvency effect, even low molar methanol fractions of $x_{MeOH} = 0.05$ and 0.10 influence the phase behaviour and VPTT of PNIPAM significantly [41]. While the VPTT decreases strongly, the shape of the $R_h(T)$ curve in these two mixtures is still similar to the one in pure water [41]. With increasing x_{MeOH} the phase transition of PNIPAM becomes broader and the VPTT decreases further. In $x_{MeOH} = 0.35$ the lowest VPTT for PNIPAM could be measured, the temperature-induced change in R_h in this mixture is already quite continuous [41]. There is a significantly reduced R_h but hardly temperature dependence detectable at $x_{MeOH} = 0.40$ [8,11,42]. The phase behaviour of PNIPAM in methanol/water mixtures is discussed in detail in Refs. [41] and [30].

Different theoretical approaches have been developed to predict the cononsolvency behaviour of linear polymers and polymer gels. The theory of preferential adsorption by Tanaka and co-workers is one of them [43,44]; it was applied successfully to PNIPAM microgels recently [41]. PNIPAM is able to form intramolecular H-bonds because its monomer unit possesses both donor and acceptor functions [45,46]. COSMO-RS [47] (conductor-like screening model for real solvents) allows the predictive calculation of chemical potentials in almost arbitrary mixtures, including polymers [48] and therefore the calculation of other thermodynamic data, e.g. liquid–liquid equilibrium, in the liquid phase. For many practical applications it already provides good predictions [49]. To our knowledge COSMO-RS has not yet been applied to model the cononsolvency of polymers or (micro) gels. Recently, Bischofberger et al. presented an experimental study on PNIPAM where they proposed the presence of two different mechanisms
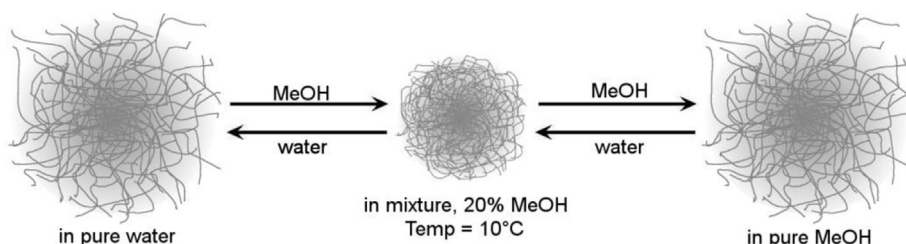

Fig. 1. Cononsolvency: PNIPAM particle in aqueous solution at 10 °C collapses upon the addition of lower alcohols (here with methanol) and swells again with alcohol excess.