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Transient-thermal and isothermal studies of thermo-sensitive polymer solution with ultrasound resonator technology

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ABSTRACT

High resolution and high sensitivity ultrasound resonator technology offers unique possibilities for the investigation of polymer precipitation. Exemplarily, the aggregation of poly(N-isopropylacrylamide) units in block copolymers with poly(styrene sulfonate) is investigated. Long term changes, over hours and days, of both the ultrasound velocity and the attenuation were detected during isothermal studies at temperatures in the vicinity (below as well as above) of the critical solution temperature. Apparent activation free energies of the precipitation and re-dissolution of the poly(N-isopropylacrylamide) block have been determined for the first time. The apparent activation energies are in the order of up to a few thousands kJ/mol, which can be explained by a high cooperativity of the precipitation process.

1. Introduction

There has been a growing interest over the last decades in thermo-sensitive polymers as smart materials for a variety of potential applications [1]. Depending on temperature these materials adjust their interaction potentials both among themselves and with their environment. Thermo-sensitive polymers in solution or in the dispersed state alter their dimensions depending on whether the interaction with the molecules of the continuous phase is getting better or worse. If this interaction decreases, the interaction between the polymer molecules increases, which eventually leads to precipitation. After changing the temperature in the reverse direction the polymer dissolves again. A so-called lower critical solution temperature (LCST) is defined where the polymer precipitates during heating and re-dissolves during cooling.

Poly(N-isopropylacrylamide) (PNIPAM) shows such a thermo-reversible LCST-behaviour in a temperature range of about 32 °C (plus or minus a few degrees, depending on the particular conditions) which is of special interest for biomedical applications. Therefore, since the first description of the precipitation of PNIPAM from aqueous solution at temperatures above 32 °C in a scientific paper in 1968 [2] this polymer became the 'working horse' in studies of thermo-sensitive properties of polymers [3–8]. Important steps in this development were the discoveries that (1) aggregation during the precipitation can be prevented by the addition of surfactants in 1978 [9] and (2) that stable PNIPAM latexes, retaining thermosensitivity, can be prepared by copolymerization with acrylamide and N,N′-methylenebisacrylamide in 1986 [10].

For some applications a sharp transition within a narrow temperature range is useful [4]. Thus, methods are needed allowing the investigation of thermo-sensitive changes within temperature gap of much less than 1 K or transient-thermal studies at various rates of temperature change. Such methods must possess a high resolution and rely on solution or dispersion properties that are reacting very fast on small temperature changes. The ultrasound resonator technology (URT) is considered to belong to the methods with an extremely high resolution in measurements of physical parameters of solutions and colloidal suspensions [11]. Recently this technique has also been successfully applied to study the thermo-reversible properties of PNIPAM solutions [12].

Another advantage of URT is the ability to carry out transient-thermal investigations. Transient-thermal studies by means of well defined heating and cooling rates allow the determination of activation energies of both the precipitation and the re-dissolution process. There are several possibilities to extract activation energies out of transient-thermal studies [13–15]. In this sense, temperature dependent ultrasonic measurement is a special kind of thermo-analysis technique and complementary to differential thermo analysis, differential scanning calorimetry, or thermo-gravimetrical analysis. With URT changes of the solution state can be easily investigated in both the transient and the isothermal modus.

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However, the drawback is that neither the ultrasound velocity nor the attenuation can easily be connected with a specific change of particular properties of the components in the system even if it contains only a single solute in an otherwise pure solvent. To the best of our knowledge results of such investigations have not yet been published for PNIPAM.

The aim of this paper is to report results on the precipitation and the re-dissolution of block copolymers made of PNIPAM and poly(styrene sulfonate) (PNIPAM-PSS) investigated under transient-thermal as well as isothermal conditions by means of URT. PNIPAM–PSS was prepared by radical heterophase polymerization technique as described elsewhere [16–18]. As the PSS blocks remain water soluble over the whole temperature range the block copolymer, which is double hydrophilic and water-soluble at lower temperatures, becomes amphiphilic at temperatures above the LCST and forms self-stabilizing colloidal block copolymer particles or micelles. The experimental data allows to determine, to the best of our knowledge for the first time, apparent activation free energies for the precipitation and the re-dissolution process of thermo-sensitive synthetic polymers.

2. Experimental information

The PSS–PNIPAM block copolymer was prepared via two stage radical heterophase polymerization and hence, it has a quite broad molecular weight distribution [18]. The molecular weight of the PSS block is between 10^5 and 1.6×10^6 g/mol (analytical ultracentrifugation) and the nitrogen to sulfur ratio in the block copolymer is 4.6 (elemental analysis, Vario micro Cube, elementar, Hanau, Germany). Hence, the PNIPAM block has a molecular weight between 3.2×10^5 and 5.1×10^6 g/mol and the overall molecular weight of the block copolymer is between 4.2×10^5 and 6.7×10^6 g/mol.

The block copolymer was dissolved in ultra-pure distilled water to result in a 0.42 wt% solution (Seral purification system PURELAB Plus™) with a conductivity of 0.06 μS cm^{-1}. This concentration gives a signal during the URT measurements while passing the LCST that can be nicely evaluated. This stock solution was repeatedly diluted until measurement of the average particle size above the LCST with routine dynamic light scattering equipment (Nicomp 370, Santa Barbara, USA) was still possible. The final solids content for dynamic light scattering was estimated to be 0.014% by weight. This low concentration guaranteed that the dynamic light scattering measurements are not influenced by interactions between the precipitated block copolymer particles. The change of the ultrasound velocity and attenuation was measured with the ResoScan URT System (TF Instruments GmbH, Heidelberg, Germany) based on URT. This instrument is equipped with ultrasonic transducers made of lithium niobate single crystals with a fundamental frequency of 10 MHz. It contains twin sample cells for sample and reference with a path length of 7 mm. They are embedded into a metal block Peltier thermostat with temperature stability of ±0.0003 K. The resolution of the ultrasonic velocity is 0.001 m s^{-1}. The ultrasound properties of the block copolymer solution are evaluated in relation to a highly diluted surfactant solution (ResoStandard, TF Instruments GmbH, Heidelberg, Germany) that practically does not alter the properties of pure water (cf. Fig. 1). All data reported are averages of at least 3 repeats. The evaluated data of URT is either ΔU (ultrasound velocity) or ΔA (ultrasound attenuation) where the delta-sign refers to the difference between the block copolymer solution and the standard. Both the ultrasound velocity and the ultrasound attenuation can be used to evaluate the data and lead to similar results [11]. The ultrasound velocity in liquids depends on the compressibility and the density of the medium. The attenuation is more complex and influenced by much more parameters (especially viscosity as well as vibration and structure relaxation processes) and hence, it is charged with larger scatter. Therefore, it is more convenient to consider the difference of the ultrasound velocity especially when diluted sample is investigated and in order to minimize concentration effects.

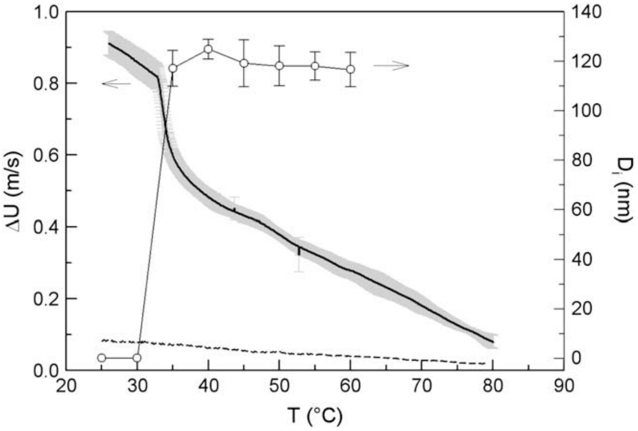

Fig. 1. Change of ΔU and D_i during the heating periods of repeated heating cycles of PNIPAM–PSS block copolymer solutions; solid line: ΔU of PNIPAM–PSS block copolymer solution (error bars grey), dashed line: ΔU of pure water, block copolymer concentration 0.42 wt%, heating rate 300 mK/min; open circles: intensity weighted average hydrodynamic diameter (D_i) after 20 min equilibration time at each temperature, block copolymer concentration 0.014 wt%.

3. Results and discussions

Thermo-reversibility of the precipitation/dissolution of the PNIPAM–PSS block copolymer is proven by the data of Fig. 1: ΔU and D_i are averages measured during the heating periods of repeated temperature scans between 25 and 80 °C.

The linear decrease in ΔU for pure water results from the difference in temperature between the reference cell and sample cell during the measurement in continuous temperature scanning modes. Briefly and simply, the temperature is recorded first, then the velocity and attenuation in cell 1 and cell 2, before the difference is calculated. There is an approximately 6 s time shift between data acquisition in cell 1 and cell 2, which correlates to a change in temperature dependent on the temperature scanning rate and the actual temperature. However, for the evaluation of the results for the block copolymer solution this inherent shift of the URT data doesn't really matter.

In contrast to the dynamic light scattering data, which 'only' allow the conclusion that in the temperature range between 30 and 35 °C particles are generated with an average hydrodynamic diameter of about 120 nm, the profile of the ultrasound velocity–temperature curve (ΔU vs. T curve) contains deeper and more detailed information about the whole process. First, there are changes over the entire temperature range indicating continuous changes with increasing temperature. This is a reasonable outcome confirming former results obtained for PNIPAM homopolymers with URT [12] and much more sophisticated dynamic light scattering studies [19]. Similar results were also obtained with microcalorimetry for symmetrical telechelic PNIPAM with octadecyl termini [20]. Second, there is a temperature range between 30 and 35 °C where ΔU changes significantly with temperature. Thus, URT and dynamic light scattering show a similar temperature range where drastic changes in the solution state of the block copolymer take place. This temperature range is typically considered as range of the LCST. For the sake of completeness, it should be mentioned that also the ultrasound attenuation (ΔA), data not shown here, varies over the whole temperature range and again with the largest alterations between 30 and 35 °C. Third, at temperatures above 35 °C ΔU changes almost with the same slope as in the range

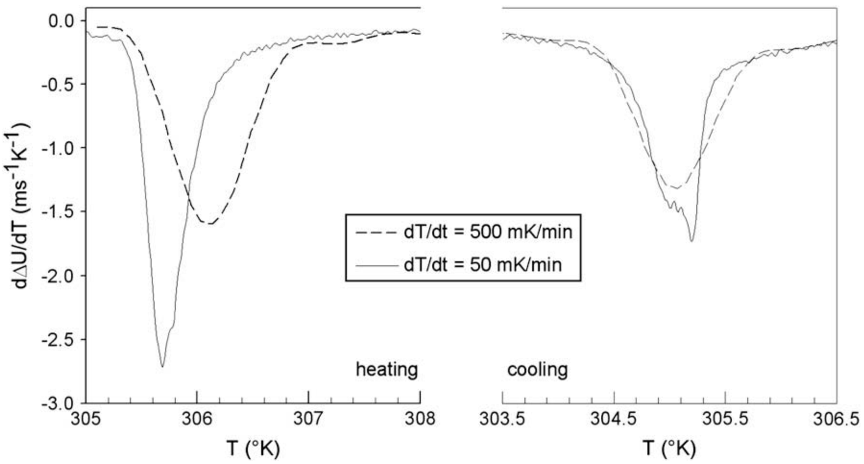

Fig. 2. Change of the temperature derivative of ΔU with temperature during heating (left hand) and cooling (right hand) for different heating/cooling rates.

between 25 and 30 °C. The ΔU-profile between 20 and 80 °C as depicted in Fig. 1 might be interpreted that increasing temperature causes gradual detachment of water molecules from the PNIPAM units until, close to the vicinity of the LCST, it is so advanced that the PNIPAM chains collapse almost catastrophically. Thereafter, at higher temperature, further changes occur in the particle water interactions. These changes above 40 °C have been interpreted as partial vitrification of the PNIPAM rich phase [12].

More information about the phase transition can be obtained considering the temperature derivative of ΔU, $d\Delta U/dT$, in dependence on temperature. Fig. 2 shows exemplarily the behavior for two different heating and cooling rates (dT/dt). Also this data reveals interesting features of the hydrophilic–hydrophobic transition of the PNIPAM units in the block copolymer. First, the temperature where the derivative of both the heating and the cooling curves has an extreme value depends on the rate of the temperature change. Second, there is a hysteresis between the heating and the cooling curves in a way that the extreme value of $d\Delta U/dT$ during cooling is shifted towards lower temperatures.

Moreover, the shape of the derivative curves for both heating and cooling depends on the magnitude of dT/dt. For values equal to or lower than 250 mK/min the curves exhibit shoulders and appear much more unsymmetrical than those at faster temperature changes. The influence of the rate of the temperature change is detailed with the data summarized in Fig. 3. The precipitation temperature (T_p determined from the extremum of $d\Delta U/dT$ during heating) and the dissolution temperature (T_d determined from the extremum of $d\Delta U/dT$ during cooling) decreases and increases with lower rates of the temperature change, respectively. However, T_p can be considered as almost constant for dT/dt values lower of about 150 mK/min. This result is in fair agreement with results obtained with high-sensitive differential scanning calorimetry of PNIPAM hydrogels showing that the transition temperature, the transition enthalpy, and the peak width increase with heating rate. Moreover, heating rate above 125 mK/min causes perturbations related to the instrument response and the kinetics of phase transition [21].

Contrary to T_p, the dissolution temperature increases also for the lowest cooling rates. Consequently, the difference between precipitation and dissolution temperatures depends quite strongly on the rate of the temperature change. Evaluating this data by linear regression gives an apparent value of 0.49 K for $dT/dt = 0$ underlying the fact that transient and equilibrium (isothermal) studies lead to different results as also observed for T_p in [21]. In other words, transient-thermal investigations are nonequilibrium studies exhibiting hystereses between heating and cooling cycles as generally observed for phase separations except dT/dt is extremely small (below 1 mK/min) and the system is well mixed in order to minimize diffusion effects [22].

The data of Fig. 3 show that the LCST of the PNIPAM–PSS block copolymer is in the range between 32 and 33 °C and not much different from that of the PNIPAM homopolymer. However, for

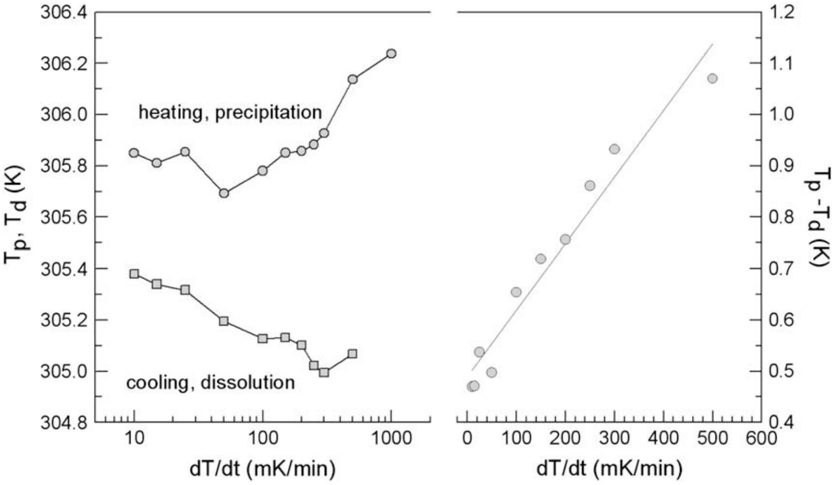

Fig. 3. Dependence of the transition temperatures (T_p, T_d) during heating and cooling cycles (left hand) and of the difference between the precipitation and dissolution temperature ($T_p - T_d$) (right hand) on the rate of temperature change (dT/dt).

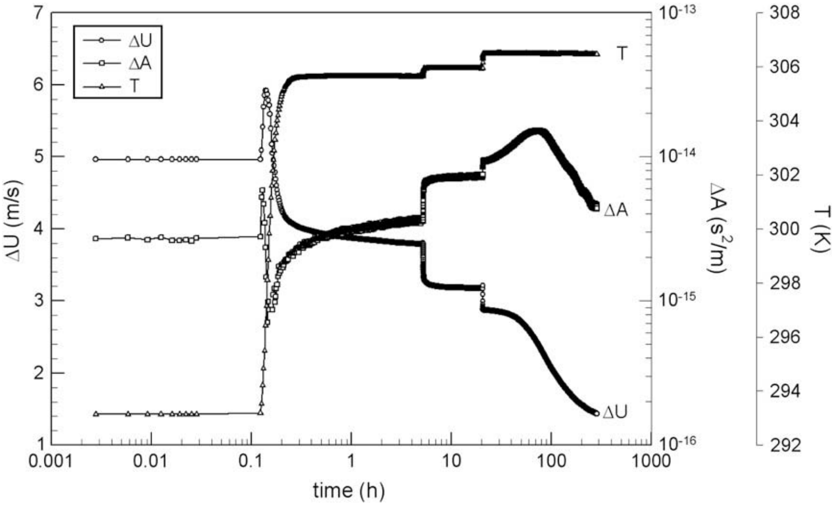

Fig. 4. Temperature jump experiments in order to follow isothermal changes of ΔU and ΔA over longer periods of time; temperature steps from 19 to 32.5 °C, 32.5 to 32.8 °C, and 32.8 to 33.5 °C.

PNIPAM-poly(acrylic acid) block copolymers (PNIPAM–PAA) with a block length ratio of 2.2 pH-dependent shifts of the LCST were observed [23]. In the pH-range 5–7 and at pH of 4.5 the LCST was 35 and 29 °C, respectively. For random copolymers of NIPAM with acrylic acid a LCST cannot be observed if the acrylic acid content is over 6 wt% and the pH is above the pK_a value [24]. In this way, PNIPAM–PSS block copolymers behave differently compared to PNIPAM–PAA block copolymers which is probably due to the possibility of intra- and intermolecular interactions between –COOH and –CONH(CH_3)$_2$ groups in the latter ones [24,23,18].

Trying to approach equilibrium, URT measurements were carried out after a jump to the desired temperature in the vicinity of T_p. Then, the changes of the ultrasonic properties of the solution (ΔU, ΔA) were followed under isothermal conditions. The result of these measurements is at a glance quite astonishing as it takes several hours or even days until more or less constant values are obtained, if so ever (cf. Fig. 4). The isothermal and the transient-thermal protocols differ principally in the fact that the latter does not allow equilibration. A temperature range of 20 K is passed through within 0.55 and 10^{-2} h for the dT/dt of 10 mK/min and 500 mK/min, respectively. Under this condition the solution has no time to relax the temperature induced stress, which is permanently renewed. In contrast, the isothermal situation gives enough time to the system to find its energetically optimum arrangement.

The general reason for the long term changes depicted in Fig. 4 is a change in the solution state of the precipitated block copolymer. Solution state means the structure of the block copolymer molecules/particle as well as the arrangement of the interacting water molecules around them. In contrast to the URT data (Fig. 4) the average hydrodynamic diameter of the precipitated particles changes only very little with time at temperatures above the LCST. Exemplarily, D_i measured repeatedly by dynamic light scattering at $T = 35$ °C within a period of time of 5 h shows 10 min after placing the sample almost no trend and gives an average diameter of 125.1 nm with a standard deviation of 3.6 nm. This different behaviour observed with both methods is reasonable. The hydrodynamic diameter as measured by routine dynamic light scattering is mainly determined by the number of chains per particle and much less influenced by both the conformations of the chains in and the density of the core as well as by the number of interacting water molecules. However, these latter points are really important for the ultrasound velocity in the sample solution and dispersion, respectively, depending on temperature.

The data presented in Figs. 1–4 reveal that the precipitation of PNIPAM–PSS block copolymers is characterized by a variety of processes taking place on quite different time scales. Especially at temperatures slightly above T_p, during the vitrification period, the ultrasonic properties of the dispersed block copolymer particles change under isothermal conditions over a period of several days. Unfortunately, these alterations cannot unambiguously be directly connected with structural changes either inside the hydrophobic PNIPAM – cores of the block copolymer particles, the hydrophilic PSS – shells, or the water structure in either of these phases. Another important factor that might influence the long term behaviour could be the polydispersity of the overall chain length distribution and the chemical inhomogeneity regarding the ratio of both blocks in the particular block copolymer made by 'normal' radical heterophase polymerization. This chemical inhomogeneity can cause shifts in the precipitation temperature of molecules with different block length compositions. In order to get an idea about this effect the comparison with a homopolymer of PNIPAM might be helpful. Both T_p and T_d are for the homopolymer larger by about 0.36 K at 300 mK/min heating and cooling rates and concentrations above 0.1 wt%. However, based only on this data, the significance of this difference on the long time behaviour as depicted in Fig. 4 for molecules that differ in the block composition cannot be judged. Nonetheless, the long time scales point to processes with either high activation energy or low frequency factors within the frame of the Arrhenius relation [25].

Activation energies or reaction orders can conveniently be extracted from transient-thermal measurements [13–15]. Since it has been argued that the differential method according to Friedman is advantageous to other methods using peak maxima [26–28], the experimental URT data have been treated in this way. This type of analysis is usually applied to thermogravimetrically obtained data over quite a broad range of temperatures. Thermal decomposition of polymers can be considered as the transition of a solid into another solid accompanied by the release of small molecules to the gaseous continuous phase. The LCST behavior of the PNIPAM–PSS block copolymer is qualitatively comparable as vitrification of the polymer goes along with the release of bound water molecules to the continuous aqueous phase. Assuming that the change of ΔU is proportional to the state of the block copolymer in the solution at given temperature it is possible to define a conversion of the transition by normalization as given by equation (1). ΔU_0 is the value at the point in the ΔU/dT versus T curves where ΔU/dT starts to change drastically and ΔU_E is the value where it returns to constant region (cf. Fig. 2).

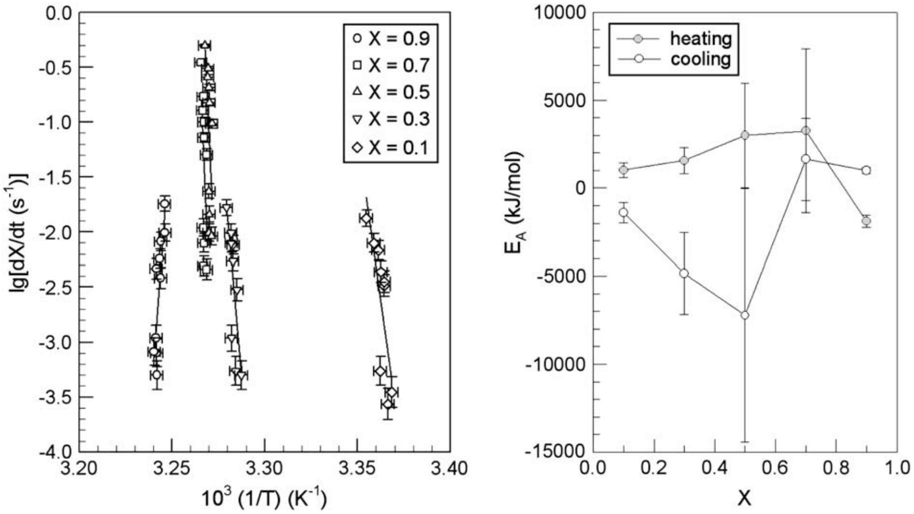

Fig. 5. Isoconversion Friedman plots for heating PNIPAM–PSS solution (left hand) and dependence of the apparent activation energies during heating and cooling on conversion (right hand); (The error bars for the activation energies have been estimated in the following way. In order to increase the statistical significance, 50 data points were randomly generated with a Monte Carlo procedure using the results of the linear regressions lg(dX/dt) vs. 1/T (left hand graph). With these data points a least squares regression of 1/T vs lg(dX/dt) was performed. From an analysis of variance (ANOVA) procedure, the standard error was estimated according to [30].)

The conversion, X, was calculated from the ΔU data between about 20 and 40 °C for the different heating and cooling rates according to equation (1) where ΔU_0 is the value at the starting temperature (either 20 or 40 °C), $\Delta U(T)$ is the value at the particular temperature or time, and ΔU_E is the value at the end temperature. The conversion rate dX/dt can be expressed according to equation (2), with a temperature-dependent rate constant $k(T)$ possessing an Arrhenius-type of activation energy E_A and an arbitrary function $f(x)$. For the Friedman analysis follows equation (3) where a plot of the logarithm of the conversion rate at equal conversions for different heating rates versus reciprocal temperature should be linear allowing the determination of E_A without any detailed knowledge about the mechanism of the transition.

$$X = \frac{\Delta U_0 - \Delta U(T)}{\Delta U_0 - \Delta U_E} \tag{1}$$

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k(T)\cdot f(x) \tag{2}$$

$$k(T) = A\exp\left(-\frac{E_A}{RT}\right)$$

$$\lg\frac{\mathrm{d}X}{\mathrm{d}t} = \lg A + \lg[f(x)] - \frac{E_A}{RT} \tag{3}$$

This analysis is very sensitive to experimental scatter since instantaneous rate values are evaluated. Additionally, due to the small temperature range of about 1 K and the narrowness of the dX/dt range, many data points are close to the maximum where the slope of the Arrhenius-plot tends to diverge. Nevertheless, the quality of the data seems good enough to extract apparent activation energies (cf. Fig. 5, left part).

As already suggested from the isothermal results, the calculated apparent activation energies are indeed extremely high. Moreover, these values depend on both the conversion and the direction of the temperature change, that is, dissolution during cooling has higher absolute values than precipitation upon heating. The conversion dependence of E_A suggests that the nature of the reaction changes with conversion. This is absolutely reasonable as at least two reactions must take place: dehydration or hydration and precipitation or dissolution during heating and cooling, respectively. Dehydration alone can proceed with altering activation energy as shown by thermogravimetric investigation of the dehydration of ferric chloride hydrate [29] where E_A changes almost by a factor of two between $0.1 < X < 0.9$.

Interestingly, for both heating and cooling the apparent energy of activation changes its sign at a high conversion that is close to the precipitation and close to the re-dissolution, respectively. At the moment there is no possibility to decide whether this effect has a mechanistic origin or is an artefact due to data quality. Despite all problems it should be mentioned that the Ozawa–Flynn–Wall analysis with the approximation of Doyle [31,15] confirms the data shown in Fig. 5. Also Kissinger's analysis gives average apparent activation energy over the whole conversion range of about 1190 and −4200 kJ/mol for heating and cooling, respectively. Again, these values are quite high and might be considered as physically unreasonable, at least for reactions involving only single molecular steps. In general, the apparent E_A – values as depicted in Fig. 5 are an expression of the overall energy that is needed for the transition from the initial to the final state. A possible reason leading not to correct but apparent values might be that the effect of the corresponding back reaction, which corresponds to a thermodynamic inhibition, is not considered as discussed in [32]. Phase transition, also the precipitation of PNIPAM–PSS block copolymer described here, is in its physical nature a nucleation and growth process. Differential scanning calorimetry of phase transition in solid explosives resulted in apparent activation energies of up to above 300 kJ/mol [32,33]. Even higher values of up to 1300 kJ/mol have been determined for collagen denaturation [34]. Such high E_A – values are explained with a cooperative action of much more than a single unit of the molecule during the transition. The acting unit is defined as 'cooperativity unit' which undergoes the transition as a whole (a type of 'all – or – none' process) [35]. The cooperativity assumption on the one hand explains in a reasonable way the high values of E_A and on the other hand allows much lower values for single molecule transitions, such as detachment of single water molecules or interaction between single monomer units.

The cooperativity of PNIPAM precipitation was also concluded from scanning calorimetry investigation where the ratio $\Delta H^{\mathrm{cal}}/\Delta H^{\mathrm{eff}}$ corresponds to the number of cooperatively acting units per molecule [36]. ΔH^{cal} is the total area of the transition peak under the heat capacity–temperature curve and ΔH^{eff} is basically the effective temperature interval around the temperature of the heat capacity maximum where the transition is assumed to be completed to 50% [35,36]. For the precipitation of PNIPAM with molecular weights between 10^4 and 3.7×10^5 g/mol in the presence of sodium dodecylsulfate an average number of 92 (±4) monomer units per cooperativity unit was determined. This means that for PNIPAM with molecular weight of about 10^4 g/mol the precipitation is all – or – none for the average molecule whereas for the polymer with a molecular weight of 3.7×10^5 g/mol about 39 cooperativity units act independently. For PNIPAM with 7×10^6 g/mol the number of monomers per cooperativity unit was found to be 600 corresponding to about 120 independent units per molecule doing the 'all – or – none' transition [37]. The amount of sodium dodecylsulfate relative to the mass of PNIPAM, which was altered in this study between 1 and 4, has obviously no influence on the cooperativity. Also, in another study from microcalorimetry data, it has been concluded that for PNIPAM and poly(N,N-diethylacrylamide) with molecular weights below 10^4 g/mol the number of repeat units per cooperativity unit can be greater than the chain length of single macromolecule, that is, more than only one chain can act cooperatively [38].

The idea of cooperativity units can also be applied for the PNIPAM–PSS block copolymers studied here to understand the high apparent activation energies. Additionally, the highly charged PSS block might also influence the transition as repulsion between the polyelectrolyte blocks should counteract aggregation. However, this effect cannot be really strong as the transition temperatures (T_p, T_d) are in the 'normal' range as observed for pure PNIPAM. Obviously, the hydrophobic attraction of the 4–5 NIPAM units per styrene sulfonate group is on average stronger than the repulsion, even if for polyelectrolyte chains the repulsion potential is longer ranging than for single charge [39].

In conclusion, URT is nowadays a powerful tool to study thermoreversible phase transition in solution either in isothermal or transient-thermal mode. It is, in addition to sizing techniques (light scattering) and calorimetry, a complementary method for comprehensive studies revealing particular features of the phase transition. The technique is sensitive enough to determine apparent activation energies of the phase transition even over a temperature range below 1 K. The data obtained for a particular PNIPAM–PSS block copolymer confirms calorimetric results showing that the transition is characterized by cooperativity effects. Under isothermal conditions the results clearly prove long-term changes in aggregate structure over several days.

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