Water uptake of hydrophilic polymers determined by a thermal gravimetric analyzer with a controlled humidity chamber

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The moisture uptake of several water-soluble polymers at different humidities was investigated with a thermal gravimetric analyzer equipped with a controlled humidity chamber. The water sorption of poly(acrylic acid) sodium salt, poly(ethylene glycol) and silica, which are known as super absorbers, were examined. In addition, various hydrophilic polymeric materials were selected according to their structural features. These included hydroxyl functions on the side chains (e.g. poly(2-hydroxyethyl methacrylate)), as well as acidic or basic functionalities (e.g. poly (dimethylaminoethyl methacrylate) or poly(vinylimidazole)). In addition, poly(2-methyl-2-oxazoline) (P(MeOx)) and poly(2-ethyl-2-oxazoline) (P(EtOx)), which are well-known hydrophilic polymers, were also investigated in this context. More significant weight percent changes were obtained for P(MeOx) (60% at 90% relative humidity (RH)) in comparison to P(EtOx) (35% at 90% RH) as a result of the slight difference in hydrophilicity of the structures. The effect of the chain length on the ability for water uptake was also investigated for both poly(oxazolines). Finally, thermoresponsive polymers with a lower critical solution temperature (LCST) behavior (e.g. poly(N-isopropylacrylamide) and poly(dimethylaminoethyl methacrylate)) were also examined. The measurements for the latter polymers were performed below and above the LCST of each polymer whereby the humidities are varied from 0 to 90% with steps of 10%. Upon increasing humidity, the results revealed relatively high water uptake values (8% and 22% for P(NIPAM) and for P(DMAEMA), respectively) below the LCSTs of the polymers and, contrastingly, a small weight loss above their LCSTs. The present results allow a deeper insight into important structure–property relationships (e.g. the influence of the polymer backbone, functional groups, LCST behavior, etc. on the water-uptake properties), and will in subsequent steps permit the directed design of tailor-made polymers for selected applications.

Introduction

For many decades, polymers have attracted great attention because of their advantageous material properties. Nowadays, polymers are used in a wide range of applications, i.e. in automotive, construction, electronic, cosmetic and pharmaceutical industries. Polymeric materials can be prepared by various polymerization techniques, including anionic,[1] cationic,[2,3] or radical[4–7] processes. Their properties (e.g. mechanical, thermal and structural) can be analyzed by a variety of characterization tools, which allows the determination of structure–property relationships.[8,9] Today, advanced characterization tools such as gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) spectroscopy, nanoindentation, thermogravimetric analysis or contact-angle measurements are routinely used for the determination of several polymer properties. A less investigated, but very important polymer characteristic that plays a crucial role in several applications of polymers such as personal care products,[10–12] coatings, composite materials, cement,[13] membranes and sensors,[14] agriculture,[15–19] biomedical,[20–22] insulation of underwater cables[23] or recreational activities (artificial snow)[23] is the moisture uptake of the materials. This property has arisen considerable interest due to its relationship with the broad range of applications. Researchers have focused on the modification and optimization of polymers in terms of water absorbency, absorption–desorption rates and gel strength (in cross-linked systems).[24–26] Moisture uptake can be measured directly from water or from a humid atmosphere. However, most of the reported research has focused on the investigation of cross-linked polymer systems (super absorbent polymers) in direct contact with water.

There are many known polymers with a variety of structures and/or functionalities that show interesting as well as industrially important water-uptake characteristics. For instance, hydrogels represent an important class of materials that are generally formed by cross-linked networks and have an ability to absorb considerable amounts of water. One of the most commonly used methods for the determination of the amount of water absorbed in cross-linked systems is a swelling

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test, which requires the network to be in direct contact with water.[27] However, this technique is not applicable for non-cross-linked systems such as linear or star-shaped hydrophilic polymers since these are often powders or liquids and would therefore dissolve in water. The water sorption of polymer films from air can be determined by using electro-microbalances. Gavara *et al.*[28] investigated the sorption and transport properties of water through films of Nylon-6 with this technique. Other instruments that measure the water uptake of materials from air are permeation analyzers,[29] dynamic vapor sorption instruments,[30] infrared near-field scanning optical microscopes,[31] stress analyzers,[32] and quartz crystal microbalances.[33] Alongside these techniques, other research groups have used desiccators conditioned at specific humidities in which the samples were weighed at specific time intervals in order to determine the water-uptake ability of the polymers.[34,35] The main drawbacks of these methods include their requiring extensive measurement periods, difficulties in controlling the temperature and related handling errors.

In the present study, the water-uptake behavior of several classes of polymers was investigated by using a thermogravimetric analyzer equipped with a controlled humidity chamber. The main advantage of this type of measurement setup was that only a relatively small amount of sample (2–3 mg) was required without any extensive sample preparation methods (the quartz crystal microbalance analyzing technique uses a similar amount of material, but requires the deposition of thin polymer films on the quartz-crystal sensor[33]) thus allowing the material to equilibrate more rapidly at various relative humidities and, consequently, significantly shortening the measuring time. The temperature was controlled by Peltier elements and was therefore easily varied.

The main goal of this work was to investigate the water-uptake ability of different classes of hydrophilic polymers at various humidities by using a thermogravimetric analysis (TGA-HC) system. The study was focused on the effect of certain functional groups on the water uptake properties of the polymers. A range of hydrophilic polymers with different properties, such as acid functions (poly(acrylic acid) (P(AA)) or hydroxy groups (poly(2-hydroxyethyl methacrylate) (P(HEMA))) were investigated. Other common water soluble polymers were also examined, including poly(vinyl imidazole) (P(VIM)) and poly(ethylene glycol) (PEG). These investigations were followed by the determination of the effect of the chain length on the water-uptake ability of poly(2-methyl-2-oxazoline) (P(MeOx)) and poly(2-ethyl-2-oxazoline) (P(EtOx)), which are known as hygroscopic polymers. Finally, the water-uptake ability of polymers with a lower critical solution temperature (LCST) behavior, *i.e.* poly(*N*-isopropylacrylamide) (P(NIPAM)) and poly(dimethylamino-ethyl methacrylate) (P(DMAEMA)), were also investigated. These measurements were carried out below and above the respective LCST of each polymer.

Experimental

Materials

P(AA) sodium salt, P(AA) and silica were purchased from Aldrich, PMMA and PEG polymer standards were obtained from PSS. P(DMAEMA) and P(NIPAM) were synthesized *via* the RAFT polymerization technique as reported elsewhere.[36,37] P(HEMA) was synthesized *via* RAFT polymerization and the RAFT agent was cleaved by using hexylamine after the polymerization. P(MeOx) and P(EtOx) were prepared by a living cationic ring-opening polymerization as previously reported.[38] P(VIM) was synthesized by free-radical polymerization according to the procedure described by Tan and Sochor.[39] All corresponding molecular weights and polydispersity indices are listed in Table 1. The investigated polymers are measured as powders that were pre-dried in a vacuum oven. Distilled water was used for the humidity chamber.

Instrumentation

The water-uptake measurements of the polymers were investigated on a Q5000 SA thermogravimetric analyzer from TA Instruments containing a microbalance in which the sample and reference pans were enclosed in a humidity and temperature controlled chamber. The temperature in the Q5000 SA was controlled by Peltier elements. Dried N_2 gas flow (200 mL min^{-1}) was split into two parts, of which one part was wetted by passing it through a water-saturated chamber. The desired relative humidity (RH) for the measurements could subsequently be obtained by mixing proper proportions (regulated by mass-flow controllers) of dry and wet stream. A schematic representation of the instrumental setup is shown in Fig. 1.
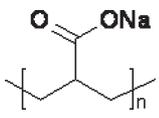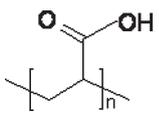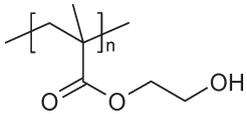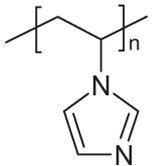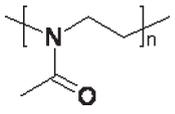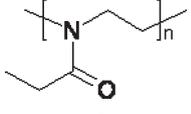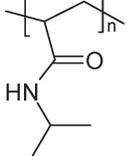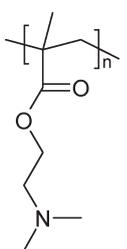
Standard measurement procedure

The standard isotherm measurement consisted of a number of subsequent steps. First, the sample was dried at 60 °C and 0% RH for a specific time until the weight change was stabilized to be less than 0.05% for a time period of 60 minutes. In the second step, the temperature was decreased to 30 °C. The humidity was then increased stepwise (with steps of either 10 or 20% RH) to a maximum of 90% RH. The weight change of the sample was stabilized after each step until it was smaller than 0.05% for a time period of 60 minutes. For some polymers the reverse isotherm was also measured. In this case the humidity was decreased down to 0% (in steps of 10 or 20% RH) and the samples were allowed to stabilize after each step. In order to finalize the isotherm and to compare the results with the initial weight of the sample, an additional drying step was included (60 °C at 0% RH).

Results and discussion

Prior to the water-uptake measurements of the polymer samples, a calibration of the humidity control chamber of the TGA was carried out by measuring the deliquescence point for a standard material. Specific salts (such as sodium bromide or lithium chloride) absorb very little amounts of water while increasing humidity until the humidity reaches a 'critical' (deliquescence) point. At this specific relative humidity and temperature, the material starts to absorb moisture from the environment. During the calibration measurement, the humidity was raised above the onset of deliquescence and then stepped down.[40] The maximum point in the negative weight

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Table 1 Selected properties of the studied polymers

Name	Structural unit	Particle size	M_n/g mol^{-1}	PDI	Weight change (%) 90% RH @ 30 °C
P(AA) sodium salt		<1000 µm (99%)			88
Silica	SiO$_2$	2–5 mm			26
PEG			2 800	1.09	73
P(AA)			1 800		33
P(HEMA)			20 600	1.31	30
P(VIM)			100 000[a]		40
PMMA			4 000	1.06	0.06
P(MeOx)			3 000	1.12	60
			11 100	1.19	63
P(EtOx)			3 000	1.14	35
			10 000	1.16	37
P(NIPAM)			50 100	1.72	8 (@ 20 °C)
P(DMAEMA)			9 500	1.11	20
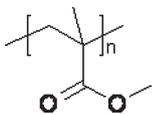
[a] Molecular weight according to ref. 39.

percent change is known as the deliquescence point. For sodium bromide, this value has been reported as 57.6 $\pm$ 2% RH at 25 °C.[40] As displayed in Fig. 2, the maximum change in weight percentage corresponds to a humidity of 58% RH which is within the error range of the reported value and thus proves the accuracy of the system.

The main point of interest of this study was the determination of the water uptake for various water-soluble polymers, including both commercially available as well as tailor-made materials, at various humidities and at a certain temperature. All the investigated polymer samples were measured as pre-dried powders. Although the morphology of the polymeric
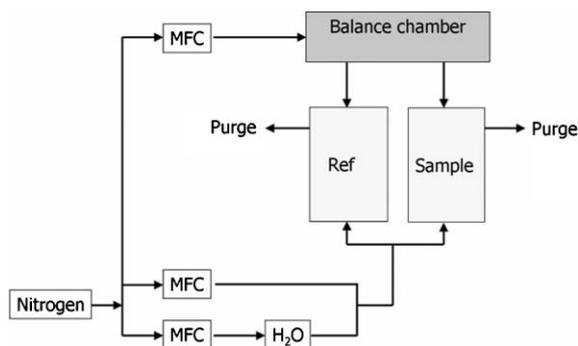
Fig. 1 The experimental setup for the thermogravimetric analysis with a controlled humidity chamber. A pre-dried nitrogen flow was split into two parts. One part of the gas stream was wetted and the desired relative humidity could be achieved by regulating proper proportions of the dry and wet streams with mass-flow controllers.

samples might strongly affect the water-uptake kinetics, it is assumed that the total absorbed moisture is less dependent on the morphology since the shape of the polymers will change (*e.g.* into viscous oil) during the measurement due to the plasticizing effect of the absorbed water. The drying process of the samples prior to the actual measurement was found to be a critical step. Therefore, during the first step of the measurement the polymer was heated to 60 °C at 0% RH until the weight change was smaller than 0.05% for a time period of 60 minutes. Thereafter, the temperature was set to the desired value and the humidity was increased in steps of 10 or 20% RH up to a maximum of 90% RH. Such a procedure yielded a complete isotherm at the specific temperature and provided water-uptake values at all different RHs. A typical plot obtained from such measurement is illustrated in Fig. 3 for silica.

Fig. 3 can be divided into five zones, A, B, C, D and E, which will be used for further explanation of the measurements. The first section of the graph (zone A) corresponds to

Fig. 3 An isothermal measurement of silica in the TGA-HC system. The first step involves a drying process at 60 °C and 0% RH (A) until the weight change was stabilized. Subsequently, the humidity was increased from 20% up to 90% RH (in steps of 20% RH) (C). In the next step (D), the RH was reduced from 90 to 10% RH in steps of 20% RH. The final procedure involved drying in order to achieve the initial weight (E).

the drying step at 60 °C and 0% RH. Initially, the weight of the sample decreased slightly and the remaining weight after 200 minutes was used to calibrate the weight change. In the next step (zone B), the temperature and the relative humidity were adjusted to 30 °C and 10%, respectively. Consequently, the weight of the sample increased up to its saturation at these specific conditions. If the weight change at these conditions was smaller than 0.05% for 60 minutes, the humidity was then further increased in steps of 20% RH up to a maximum relative humidity of 90% (zone C). Subsequently, the humidity was decreased in steps of 20% RH to a final humidity of 10% RH (zone D). In order to finalize the isotherm, an additional drying step (zone E) was included to validate the measurement by comparing the initial and final sample weights. From these plots, the equilibrated weight percent changes were extracted at different RHs and were used to plot the sorption isotherms (Fig. 4).
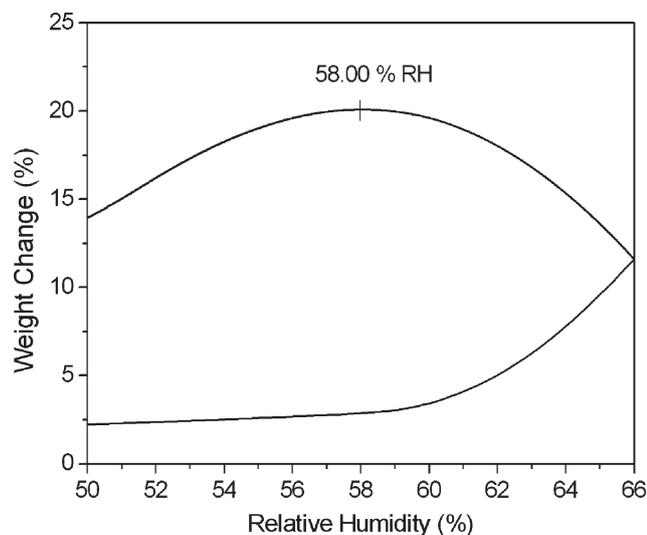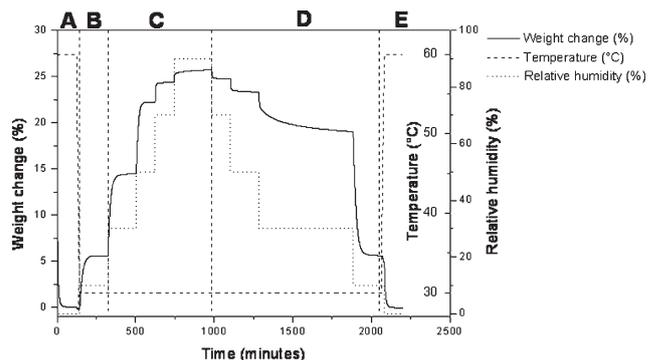

Fig. 2 A measurement of the deliquescence point of sodium bromide in order to determine the accuracy of the TGA-HC system. The maximum point in the weight change is considered to be the deliquescence point.
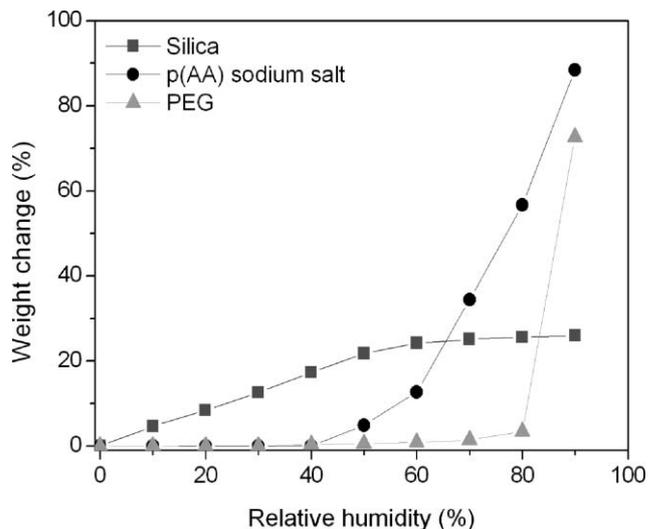

Fig. 4 Water-uptake measurements of P(AA) sodium salt, poly(ethylene glycol) and silica, demonstrating the weight change (%) as a function of the relative humidity (%) for each sample (sorption isotherm).

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Poly(acrylic acid) (PAA) sodium salt, poly(ethylene glycol) (PEG) and silica are known as "super absorbent" materials, and are used in diapers, personal care products or as drying agents. More specifically, as a super absorbent polymer, the P(AA) sodium salt has the ability to absorb up to 500 g of water per gram of polymer.[41] They thus reveal a remarkable capability to bind water molecules when immersed directly in water. Hence, the standard measurement procedure was applied for these super absorbent materials in order to investigate their water-uptake behavior when they were in a humid atmosphere and not in direct contact with water. The obtained weight percent change of these materials at different RH values (sorption isotherm) is plotted in Fig. 4. The P(AA) sodium salt exhibited the highest water uptake at 90% RH (88%) as compared to PEG (73%) and silica (26%). However, P(AA) sodium salt and PEG displayed smaller weight changes than silica at low humidity levels. The weight change of silica increased in a relatively linear fashion until it reached its maximum sorption level. In the case of PEG, the material did not absorb any significant amounts of water until the humidity level reached 80% RH, but at 90% RH, the weight change recorded was as high as 73% after stabilization. The good solubility of PEG in water is based on the distance between the alternating oxygen atoms in PEG chains that is in a similar range as the hydrogen distances in water allowing the formation of an extensive hydrogen-bonding network with water. However, solid PEG crystallizes, which obstructs the penetration of water molecules and thus the water uptake. Therefore, it is proposed that when at high RH a first hydration shell is formed in the PEG, the PEG chains will adapt the desired conformation of the polymer chains to be able to form extensive hydrogen bonds with water, favoring the uptake of more water. A similar effect can be seen in the non-linear uptake behavior of all investigated polymers, which might also be explained by the difficulty in forming a first hydration shell that extends the polymer coils. To overcome this negative entropy effect a certain amount of favorable polymer–water hydrogen bonds (hydration shell) needs to be formed. The subsequent hydration shells are more easily formed due to a smaller entropy effect and, thus, a steep increase in water uptake is observed at high RH values.[42,43] However, silica did not obey this proposed mechanism, *i.e.* it becomes saturated at lower humidities as compared with the other materials, which might be due to a different water-uptake mechanism since the solid cross-linked silica particles cannot easily swell obstructing the formation of several hydration shells. In summary, these water-uptake results demonstrate that super absorbers behave very differently when they are exposed to direct contact with water or to humid atmospheres.

In addition to the analysis of the super absorbers, a set of water-soluble polymers (*i.e.* P(AA), P(HEMA) and P(VIM)) with various functionalities was analyzed. PMMA was also included in this set of polymers to confirm that no significant amount of water was adsorbed in the sample pan and to demonstrate the poor interaction between water molecules and this hydrophobic polymer. The obtained sorption isotherms for these measurements are displayed in Fig. 5. As expected, PMMA revealed a weight change of less than 0.1% during the complete measurement cycle. The maximum measured weight
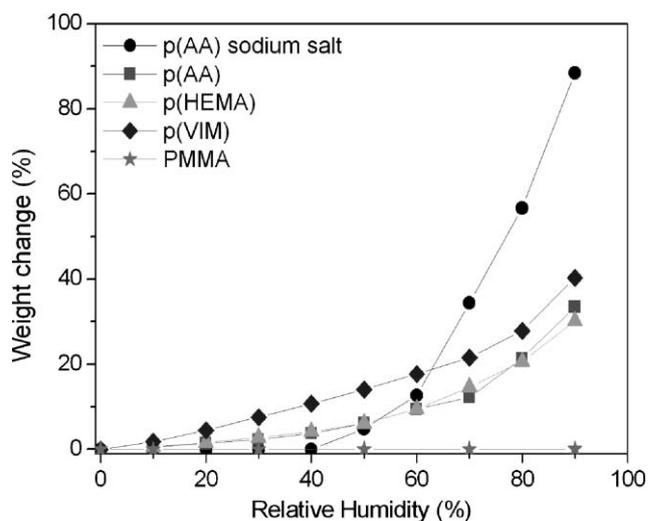

Fig. 5 Water-uptake measurements of P(AA) sodium salt, P(HEMA), P(VIM) and PMMA demonstrating the weight change (%) as a function of the relative humidity (%) for each sample.

percent change corresponded to the P(AA) sodium salt (88%), which was more than twice the measured value of P(AA) (34%). The sorption isotherms of P(AA) and P(HEMA) were found to be very similar with maximum water uptake values of 34% and 31% at 90% RH, respectively. In contrast, the investigated P(VIM) showed higher water uptake values at all humidities (except for the case when compared with the P(AA) salt at high humidity), whereby the mass change increased linearly up to 70% RH. The similar water-uptake behavior of P(AA) and P(HEMA) could be rationalized by the presence of the hydroxy and acid groups in both polymer backbones. In general, the ability of polymers to absorb water is due to the presence of hydrophilic groups such as –OH, –NH$_2$, –CONH–, –CONH$_2$, –COOH and –SO$_3$H.[44,45] These groups are able to act as hydrogen-bond donors for water, while the carbonyl groups from the acid moiety of the P(AA) and the ester moiety of the P(HEMA) are known as the primary H-bond acceptors.[44,45] Thus, both polymers display similar interactions with water, which might be related to the formation of similar hydration shells and, therefore, a similar water-uptake behavior. Compared to these polymers, P(VIM) has stronger hydrogen-bond accepting groups with respect to the carboxylic acid and the ester groups as donor groups resulting in a higher water uptake.

The TGA-HC investigation was also carried out on two poly(2-oxazolines), *i.e.* P(MeOx) and P(EtOx). These polymers contain amide groups with a carbonyl group in the side chain and a nitrogen group in the backbone. P(MeOx) and P(EtOx) are both water soluble. The water uptake values for both cases were measured for samples with a relatively low degree of polymerization (30 units), so that the effect of the substituents on the backbone (methyl or ethyl) should be directly responsible for any observed difference. The resulting sorption isotherms are depicted in Fig. 6. It can be seen that the P(MeOx) has the ability to absorb 60% of water at 90% RH, while the P(EtOx) absorbs only 35% under equivalent experimental conditions. Both polymers contained hydrogen-bond
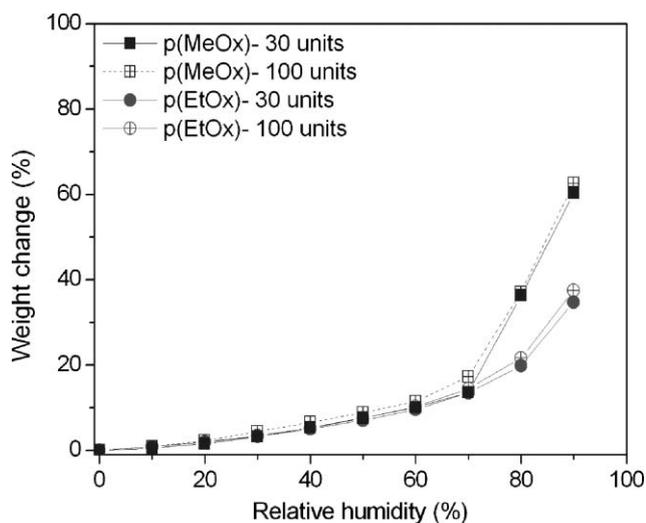
Fig. 6 Water-uptake measurements of P(MeOx) and P(EtOx) with varying chain lengths, demonstrating the weight change (%) as a function of the relative humidity (%) for each sample.

accepting groups, which explains their relatively high water-uptake values. The smaller fraction of hydrophobic side chains in P(MeOx) rendered it more hydrophilic and P(MeOx) could therefore absorb more water at high humidities than P(EtOx). In addition, the effect of the chain length on the water uptake was also investigated for these polymers. For this purpose, P(MeOx) and P(EtOx) polymers with 100 repeating units were used. As displayed in Fig. 6, the P(MeOx) with 100 repeating units showed a water-uptake ratio that was only slightly higher than for its counterpart with only 30 repeating units. A similar effect was observed for P(EtOx). These results indicate that the effect of the chain length on the water-uptake of these polymers was practically negligible. However, to be able to fully judge the effect of chain length on the water-uptake, future investigations will focus on a broader molecular weight range as well as on the effect of chain length for other polymers.

Thermoresponsive polymers exhibiting a lower critical solution temperature (LCST) in aqueous medium are very promising materials for various bioapplications, *e.g.* enzyme recycling, protein chromatography, controlled bioadhesion, hyperthermia-induced drug delivery or tissue engineering.[46] The LCST behavior is related to a delicate balance of hydrogen bonds that are formed between the polymer and water molecules and the hydrophobicity of the polymer chain. Below the LCST, the polymer chains are fully hydrated and the polymer behaves as a hydrophilic structure. The polymer is therefore soluble in water. However, above the LCST the hydrogen bonds between the water molecules and the polymer chains are broken and the hydration shell around the polymer is destroyed, thus giving rise to a hydrophobic structure. This, in turn, results in collapsed polymeric chains in solution and the polymer is precipitating. The water-uptake behavior of LCST polymers is also of great interest since such materials are expected to display different trends below and above their specific LCSTs. As a result, it should be possible to alter the water-uptake behavior by changing the temperature. P(NIPAM) and P(DMAEMA) homopolymers have been reported to display LCST values in water of 32 °C and 46 °C, respectively.[36,37] Consequently, water-uptake measurements were performed below and above the LCST temperature, namely at 20 °C and 40 °C for P(NIPAM) and at 30 °C and 80 °C for P(DMAEMA). The isotherm measurement of P(NIPAM) at 20 °C (shown in Fig. 7) exhibited a linear increase of the weight change as a function of RH and a maximum water uptake of 8% at 90% RH was recorded. This demonstrates the ability of the polymer to attract water molecules from the environment at temperatures below its LCST. A similar measurement was performed at 40 °C. At this temperature, which is above the LCST of P(NIPAM), the polymer did not absorb any water molecules. On the contrary, a negative weight change was observed rendering an apparent increase in the hydrophobicity of the polymer chain with increasing RH. A similar behavior was also observed for P(DMAEMA). The slight decrease in weight upon increasing
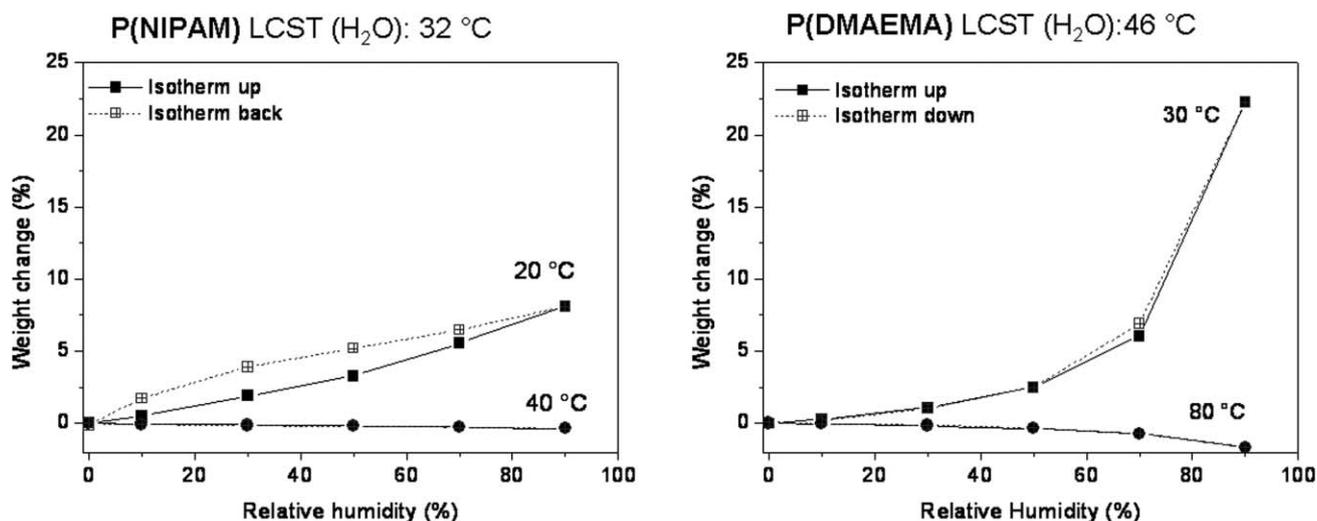

Fig. 7 Water-uptake measurements of P(NIPAM) and P(DMAEMA) below and above their respective LCSTs, demonstrating the weight change (%) as a function of the relative humidity (%) for each sample.

the RH above the LCST is not understood at this moment and will be the focus of future investigations. Furthermore, the obtained change in weight percentage for P(DMAEMA) was 22%, which is higher than for P(NIPAM) below the respective LCST. The higher water uptake of P(DMAEMA) as compared to P(NIPAM) can be explained by the fact that P(DMAEMA) was a better hydrogen-bond acceptor due to its nitrogen and carbonyl groups, which are thought to improve the formation of a hydration shell around the polymer. The reversibility of the water uptake at a constant temperature was clearly seen in the case of P(DMAEMA). The P(NIPAM) showed a slight hysteresis during the desorption measurement, performed below its LCST, which might be related to intrachain hydrogen bonding that also causes hysteresis in the LCST transition of aqueous P(NIPAM) solutions.[47]

Conclusions

In the present study, the water-uptake abilities of a number of materials were investigated by TGA-HC at various humidities. The feasibility of the well-defined, precisely controlled and now commercially available setup for these measurements was demonstrated on polymeric materials regardless of their physical form (liquid, powder or cross-linked systems). The various classes of polymers were analyzed for their water-uptake behavior under reproducible and automated conditions. At first, the water uptake of superabsorbers, more specifically P(AA) sodium salt, PEG and silica, was determined. P(AA) sodium salt and PEG showed lower water-uptake values at low humidities and higher water-uptake values at high humidities as compared to silica. The steep increase in water uptake at high RH conditions is believed to be related to a certain difficulty in the formation of a first hydration shell after which additional hydration shells could form more easily. Furthermore, other hydrophilic polymers, i.e. P(AA), P(HEMA) and P(VIM), as well as a hydrophobic polymer, P(MMA), were studied and the results were compared with those for the P(AA) sodium salt. In general, it seems that materials with hydrogen-bond accepting groups are more prone to displaying high water-uptake values as compared to materials with hydrogen-bond donor groups. This is most likely due to the facilitated formation of hydration shells around the polymer. In addition, p(MeOx) and p(EtOx) were also investigated with the TGA-HC. Although both polymers had hydrogen-bond accepting groups, the p(MeOx) was found to absorb more water at higher humidities because of its slightly more hydrophilic structure. In addition, the chain length of these poly(2-oxazoline)s was found to have almost no influence on their water-uptake ability. Finally, polymers with an LCST behavior were examined and were found to reveal different trends below and above their LCSTs. P(DMAEMA) absorbed more water in comparison to P(NIPAM) at temperatures below their specific LCSTs, and a further weight loss was observed for both materials when increasing the RH above the critical temperature.

The advanced and precise characterization tool presented in this study will be of great use for the determination of the water-uptake abilities of polymers or other materials. The experiments are carried out at controlled humidity levels and temperatures. In addition, very small amounts of sample are required. The complete setup is automated with an auto-sampler, the humidity and temperature are continuously and accurately controlled, and, as a result, the remaining handling errors are negligible. Further investigations will include the detailed study of (block) copolymer libraries (see e.g. ref. 36, 48 for selected polymer classes) with the aim of elucidating structure–property relationships and subsequently designing new polymers with tailor-made water-uptake properties, e.g. for applications in cosmetics, dryers/coolers, agriculture, drug delivery, cement, artificial snow recreational applications, insulation of underwater cables and others.

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