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Influence of the Crosslinker Hydrophobicity on the Swelling Kinetics of Poly(Acrylic Acid) Microgels

*Torsten Gereon Linder, Alima Heinzelmann, Juliane Kamphus, and Sebastian Seiffert**

Superabsorbent polymer gels are widely used in commercial areas, such as in hygiene products. A key aspect in these and other applications is the gel swelling kinetics, and a key factor of influence on that is the hydrophobicity of the gel. This paper reports on the synthesis of superabsorbent polymer microgel particles with four differently hydrophobic crosslinkers: *N,N'*-methylenebisacrylamide (MBAA), *N,N'*-ethylenebisacrylamide (EBAA), *N,N'*-propylenebisacrylamide (PBAA), and *N,N'*-butylenebisacrylamide (BBAA). This work uses droplet-based microfluidics to produce uniform and well-defined microgel specimen and study the influence of the crosslinker hydrophobicity on the swelling kinetics. In particular, this work determines swelling constants and their dependencies on the temperature of the swelling medium as well as the activation energies of swelling in relation to the crosslinker hydrophobicity. This work finds two competing effects, leading to a narrow window in which the activation energy of the swelling of the microgels decreases with increasing crosslinker hydrophobicity.

1. Introduction

Superabsorbent polymers (SAPs) are integral parts in many areas of use, such as in the field of medicine and pharmaceutics and as in disposable hygienic products.[1–3] In these and other applications, the swelling kinetics of the SAPs is of crucial importance.[1–3] As a result, research on different influences on the swelling kinetics of diverse types of SAPs has been intense, such as the influences of the SAP size, shape, and chemical composition as well as influences from the swelling medium.

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Already in 1979, Tanaka and Fillmore derived a power-law relation between the swelling time and the SAP size for spherical gels; later on, Li and Tanaka further expanded their theories in 1990 to cylindrical and disk gels.[4,5] In 2009, Atta et al. compared two crosslinkers, *N,N'*-methylenebisacrylamide (MBAA) and melaminetriacylamide, in poly(acrylic acid) and found that the latter had faster swelling ratios.[6] Furthermore, Jovanovic et al. investigated the swelling kinetics of poly(acrylic acid) hydrogels at different pH, finding that the activation energy of swelling decreased upon increase of the pH.[7] Using sodium methacrylate, methacrylic acid, and acrylonitrile copolymers, Sunitha et al. investigated the influence of the acrylonitrile on the swelling ratio, as well as the influence of the crosslinker concentration (butylene dimethacrylate) on the swelling kinetics of the hydrogels. The authors found that with increased crosslinking density, the swelling rate did increase as well. Furthermore, with increasing acrylonitrile content, the swelling ratios first decreased and then again increased (<8.9 mol%).[8] Also, Sharma and Madras studied the swelling of cationic SAPs made of [2-(methacryloyloxy) ethyl] trimethylammonium chloride and different crosslinkers with different amounts of functionalities, among which were MBAA (tetrafunctional), trimethylpropane trimethacrylate (hexafuntional), and pentaerythritol tetraacrylate (octafunctional). They found that an increase of the functionality from 4 to 6 resulted in an increase of the swelling capacity, but a further increase from 6 to 8 lead to a decrease.[9]

In general, SAPs are lightly crosslinked 3D polymer networks in which acrylic acid is the most commonly used monomer. Other common monomers are *N*-isopropylacrylamide, methacrylic acid, and ethylene oxide is sometimes also used as co-monomers with acrylic acid. As crosslinker, MBAA is the most typical choice.[6,7,10–17] The selection of the monomer as well as the crosslinker comes along with several underlying influences on the swelling kinetics, such as the possible neutralization degree of the monomer or the concentration of the crosslinker, leading to different crosslinking densities, which does not only affect the swelling kinetics, but also the mechanical properties of the SAPs. As these properties are usually predetermined in applications, influences on the swelling kinetics with no major impact on the mechanical properties are of special interest. The gel hydrophilicity and hydrophobicity can be considered as one such influence. It can be varied in several ways. One way is the integration of a co-monomer into the polymer chain backbone,

as found in the form of acrylamide-*co*-acrylic acid polymer gels or Pluronic ethers used by Bomberg et al., even though in this case no swelling kinetics was investigated.[16] Okala et al. did the same using acrylic acid, *N,N*-dimethylacrylamide, and tert-butylacrylamide among other monomers to vary the gel hydrophobicity. They found that an increase of the co-monomer in the gel lowered the rate of swelling, due to increasing hydrophobicity in the gels.[18] Another possibility to influence the SAPs hydrophilicity/hydrophobicity is the crosslinker, which often results in a direct comparison between two different crosslinkers, as it was done by Atta et al., who found that the crosslinker melamine triacrylamide showed faster swelling rates in poly(acrylic acid-*co*-*N*-isopropylacrylamide) gels than the crosslinker MBAA, which these researchers attributed to the increased hydrophobicity of the copolymers and the formation of a less elastic network.[6]

In most kinetic studies, SAP sample specimen are synthesized via a bulk method, for example in cylindrical molds, via free-radical polymerization.[6,7,18–20] Such SAPs commonly show pronounced nanoscopic network defects and structural inhomogeneities.[21,22] Also, the observed swelling times of such SAP specimen are often in the range of several hours, as commonly determined via a gravimetric approach known as the "tea bag method".[6,7,18–20,23] In this method, a dry SAP is placed in an excess of swelling solution and left to swell for a determined time. Then, it is removed from the swelling solution, and after excess medium is removed from the outside of the gel, the SAP is weighted, and the weight increase noted. This process, however, is prone to inaccuracies. One such inaccuracy is the removal of excess medium after the SAP is taken from the swelling solution, which is commonly performed with a tissue and may both be done too gently or too harshly. In addition, the typically long swelling times in the tea bag method can come along with ageing of the structure of a gel, such as hydrolysis of parts of the network. Long swelling times as well as gel hydrolysis also generally render such SAPs inapplicable for most commercial products.

On top of these practical flaws, the current level of research generally lacks a systematic isolation of the influence of the crosslinker hydrophobicity on the swelling kinetics of SAPs that leaves other influences as the concentration of the crosslinker as well as the SAPs monomer constant. Furthermore, a faster approach to determine the swelling speed is needed to quantify the influence of factors such as the network hydrophobicity.

In this paper, we aim to systematically isolate the influence of the crosslinker hydrophobicity on the swelling kinetics of SAP microgels. We keep the composition of the polymer gels consistent in both the fraction of the monomer, which is 50% neutralized acrylic acid, as well as the molar concentration of both the monomer and the crosslinker. As crosslinker, four different *N,N'*-alkylbisacrylamides are employed: MBAA, *N,N'*-ethylenebisacrylamide (EBAA), *N,N'*-propylenebisacrylamide (PBAA), and *N,N'*-butylenebisacrylamide (BBAA), as displayed in **Figure 1**. The hydrophobicity of these crosslinkers increases as the alkylene chain lengths increase. With these components, we use droplet-based microfluidics to template uniform, sub-millimeter-sized microgel specimen.[24–27] Due to efficient transfer of the heat of polymerization from the gelling droplets to a surrounding continuous phase, hot spots inside the gelling specimen are avoided, thereby reducing large-scale structural heterogeneities in the gel samples.[24,28] As the swelling time scales with the square of the size of the microgel,[4] the swelling kinetics of these small microgels can be easily observed via optical microscopy in real-time, whereby the datapoint density is only limited by the millisecond-range camera framerate.

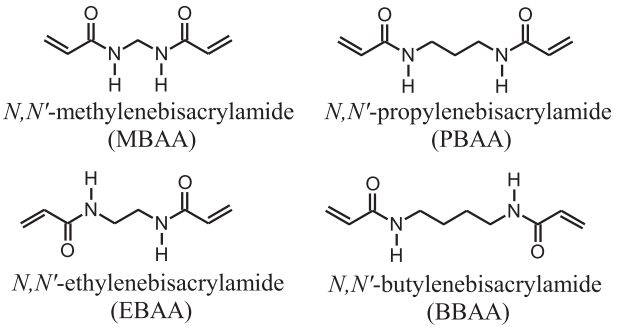

Figure 1. Crosslinkers used in droplet-based microfluidic experiments to create superabsorbent polymer microgels.

2. Results and Discussion

2.1. Reactivity Ratios within Co-Polymerization

The material basis of our work are SAP microgels of partially neutralized acrylic acid and four differently hydrophobic crosslinkers, templated by droplet-based microfluidics. The goal of our investigation is to independently assess the crosslinker hydrophobicity on the microgel swelling kinetics. This ambition requires that all four crosslinkers are chemically incorporated into the microgels with similar extent and spatial distribution. Both can be assumed to be given if their reactivity ratios are similar in the microgel co-polymerization. However, as the crosslinkers carry two reactive groups and will lead to a crosslinked product, it is difficult to determine their extent and pattern of incorporation in the final microgel by common polymer-analytical methods. To circumvent this challenge, we take a detour and determine the reactivity ratios of monofunctional analogs to the crosslinkers, as depicted in **Figure 2**. We copolymerize these with the main monomer (50% neutralized acrylic acid) at different compositions and interrupt the reaction at low conversion. Isolation and analysis of the

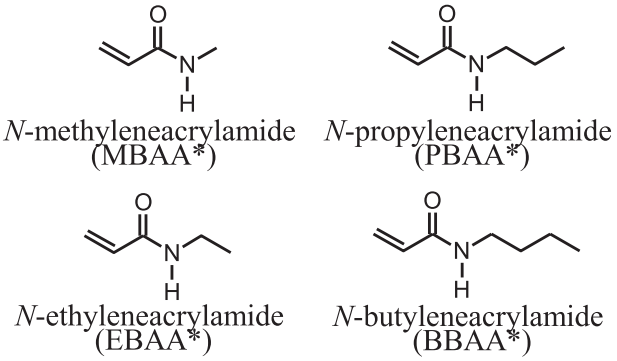

Figure 2. Monofunctional *N*-alkylacrylamides used in the determination of the reactivity ratios upon co-polymerization with acrylic acid (sodium acrylate).

resulting linear co-polymers allows us to determine the reactivity ratios and to check whether they are similar.

If the crosslinker in a co-polymerization has a higher reactivity ratio with itself than with the co-monomer, it is prone to assemble in local domains within the microgels. To check for this, we determine the reactivity ratios of the co-polymerization of 50% neutralized acrylic acid with *N*-methyleneacrylamide (MBAA*), *N*-ethyleneacrylamide (EBAA*), *N*-propyleneacrylamide (PBAA*), and *N*-butyleneacrylamide (BBAA*) from copolymers made from reaction batches with ratios of 20, 40, 60, and 80 mol% of the corresponding *N*-alkylacrylamide. We analyze the mole fraction of the *N*-alkylacrylamide in the copolymer, F_2, via ^{1}H-NMR-spectroscopy. For this purpose, the NMR-peak of the terminal methyl group of the co-monomer is put in relation to the polymer-backbone, as depicted in **Figure 3** on the left. The mole fraction of the co-monomer within the polymer is then put in relation with the mole fraction of the co-monomer within the monomer solution, f_2. The reactivity ratios of the copolymerization r_1 and r_2 are then determined through linearization of the data in accordance with the method of Kélen and Tüdös,[29] as shown on the right of Figure 3 and listed in **Table 1**.

All copolymerization reactions are performed in 20 mL milli-Q water and terminated at low conversion. During the polymerization with the co-monomer *N*-butyleneacrylamide, the monomer solution turned opaque instantly after initiation if the concentration of the co-monomer content was at least 40 mol%. This observation impaired the determination of the reactivity ratios for this co-monomer.

We find that the reactivity ratio r_1 is similar for all, MBAA*, EBAA*, and PBAA*, whereas the reactivity ratio r_2 increases as the hydrophobicity of the *N*-alkylacrylamide increases. Thus, the statistical distribution of the co-monomers in the polymer decreases as well. Nevertheless, based on extrapolation of the data, their incorporation into the copolymers is expected to be similar for all the three in the lower range of composition (<5 mol%). Hence, we conclude that the analog bifunctional crosslinkers are incorporated and distributed similarly in all our microgel samples at low mol-percentages.

2.2. Swelling Kinetic Studies

We continue our investigation with crosslinked and gelled SAP microspheres created by droplet-based microfluidics. Once dried, theses microgels with diameters between 50 and 60 µm are swollen in physiological saline solution, thereby obtaining larger diameters of around 100–200 µm. The swelling process is videotaped using a UI-3060CP from IDS camera mounted to an inverted optical microscope, and the frames are extracted via a python routine from the video and then analyzed. Some frames are displayed in **Figure 4**.

The swelling degree (SD) of the SAPs is defined from the normalized diameter of the particles:

$$\mathrm{SD} = \frac{d_t}{d_0} - 1 \tag{1}$$

In this equation, SD is the swelling degree, d_t is the diameter of the particles at the time t, and d_0 is the diameter of the particles in the dried state. Plotting the SD against the time that the SAP microparticles spent in excess physiological saline solution results in the corresponding swelling curve. We determine these curves on an individual particle level, as shown in **Figure 5**.

Fitting of the datapoints for the swelling of the SAP microspheres is best achieved with a bi-exponential function:

$$\mathrm{SD} = A \cdot \left(1 - \exp\left(\frac{-t}{\tau_1}\right)\right) + B \cdot \left(1 - \exp\left(\frac{-t}{\tau_2}\right)\right) \tag{2}$$

With A and B being weighting factors of the two exponential functions, t the time that the microgel was surrounded by swelling medium, and τ_1 and τ_2 the specific swelling times. A compilation of all fitting-parameter values is available in the Supporting Information. After each of the particles swelling curves are fitted, the average of the swelling curve fits of all particles containing one crosslinker and swelling at 10 °C, 25 °C, 45 °C, 65 °C, and 85 °C are taken. The averaged datapoints are again fitted to Equation (2), as shown in **Figure 6**.

The averaged swelling curves of the SAP microparticles containing the different crosslinkers MBAA, EBAA, PBAA, and BBAA show no clear trend as the temperature of the swelling medium increases. In general, all SAP microparticles reach the swelling equilibrium within 100 s, with extremely fast changes in the SD within the first few seconds after the microparticle is immersed in the swelling solution.

A possible model to describe the swelling kinetics is the diffusion of the gel-network as a primary driving swelling kinetic force, as expressed by Equation (3):[20]

$$\ln\left(\frac{\mathrm{SD}_{\mathrm{eq}}}{\mathrm{SD}_{\mathrm{eq}} - \mathrm{SD}_t}\right) = k \cdot t \tag{3}$$

In this equation, k is the swelling constant of the gel, $\mathrm{SD}_{\mathrm{eq}}$ the SD at equilibrium, and SD_t the SD at time t. **Figure 7** shows this function applied to the swelling kinetics of the SAP microspheres with the four different crosslinkers.

Figure 7 shows a linear relationship up to at least 90% of the swelling for all SAP microspheres once the temperature of the swelling medium is at least 25 °C. Furthermore, the influence of the crosslinker hydrophobicity also leads to an increase in the linearity at 10 °C. Therefore, it can be concluded that the rate-limiting factor of the SAP microspheres' swelling kinetics is the gel diffusion. In addition, as the hydrophobicity of the gel slightly increases for the more hydrophobic crosslinkers, this influence becomes even more prominent, especially for swelling beyond 90% of the equilibrium capacity of the microgels. Regarding the plots shown for 65 °C and 85 °C, it can further be seen that the difference of the two plots becomes less as the hydrophobicity of the crosslinker increases. As each swelling kinetic curve has its own swelling constant k, specific to the type of microgel as well as the temperature of the swelling medium, we calculate all swelling constants, as listed in **Table 2** and plotted against the temperature of the swelling medium T in **Figure 8**.

Figure 8 shows a linear relation of the swelling kinetic constant k and the temperature of the swelling medium T, which seems to start to break down and reach a plateau between 65 °C and 85 °C at higher crosslinker hydrophobicity. This finding corresponds to the previous observation in Figure 7, where the plots at 65 °C

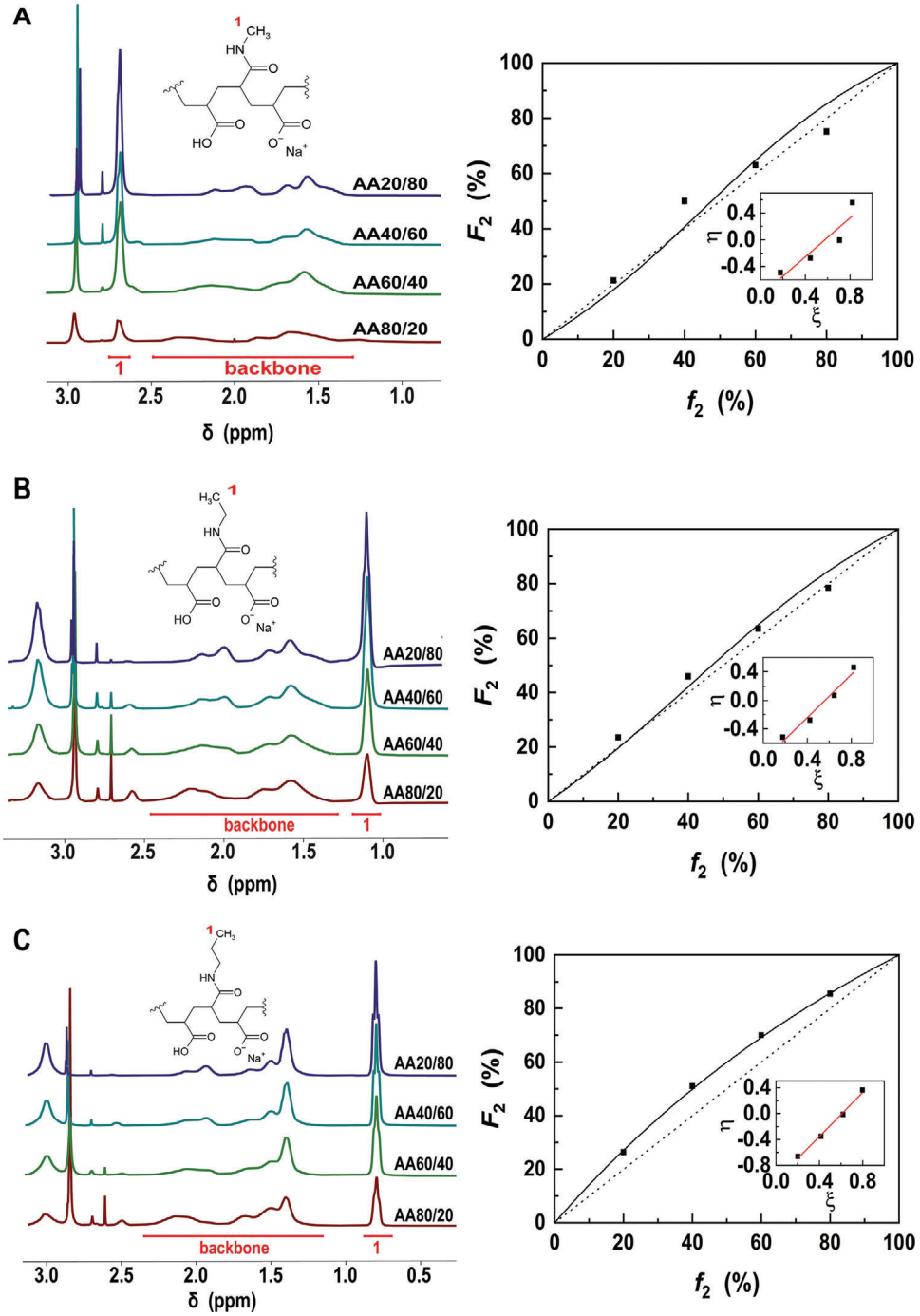

Figure 3. Left: NMR-spectra of copolymers of 50% neutralized acrylic acid with *N*-methyleneacrylamide (A), *N*-ethyleneacrylamide (B), and *N*-propyleneacrylamide (C). Right: Plot of the mole fraction of the corresponding *N*-alkylacrylamide in the polymer (F_2) versus the mole fraction in the monomer solution (f_2). The full line is calculated from the copolymerization equation using the corresponding reactivity ratios determined in this work. The inset on the right shows a linearization of the data according to the method of Kélen and Tüdös.[29]

and 85 °C become more identical as the hydrophobicity of the crosslinker increases.

If only the linear relation of the swelling constant versus temperature of the swelling medium is fitted, the change rate, Δk, can be determined, as listed in **Table 3**. We notice that with increasing hydrophobicity of the crosslinker, starting from MBAA to PBAA, the change rate decreases. As the hydrophobicity of the crosslinker further increases (BBAA), however, this trend inverses, leading to an increase of the change rate even exceeding the calculated values of the most hydrophilic crosslinker MBAA.

Based on the calculated swelling constants k of the four different SAP microgels (Table 2), the activation energies E_a of the

Table 1. Reactivity ratios of a co-polymerization of 50% neutralized acrylic acid with *N*-methyleneacrylamide (MBAA*), *N*-ethyleneacrylamide (EBAA*), or *N*-propyleneacrylamide (PBAA*).

Co-monomer	r_1	r_2
MBAA*	0.615	0.778
EBAA*	0.663	0.894
PBAA*	0.663	1.482

swelling process can be calculated based on an Arrhenius approach, as compiled in **Table 4** and **Figure 9**. In the case of the more hydrophobic crosslinkers PBAA and BBAA, the plateau region at higher temperature is ignored for the calculation of the activation energies.

The calculated activation energies of the swelling of the SAP microgels express a similar trend as the change rate of the swelling constants. At first, the activation energy E_a decreases as the hydrophobicity of the crosslinker increases. This trend again reverses for the crosslinker BBAA, as its activation energy increases in comparison to the less hydrophobic crosslinker PBAA. Furthermore, the calculated activation energy of the most hydrophobic crosslinker BBAA surpasses the activation energy of the most hydrophilic crosslinker used (MBAA).

In summary, the swelling kinetic studies of the SAP microgels synthesized in this study show that even though only a small part of the microgels' hydrophobicity is changed, there is a measurable effect on the swelling kinetics. Specifically, an increase in the hydrophobicity of the crosslinker within the SAP shows an increase of the influence of the gel-network diffusion during the swelling at 10 °C. Once the temperature of the swelling medium is at least 25 °C, the plots in all cases show almost perfect linearity. Using the linear relation of Equation (3), swelling constants can be calculated from which the change rate of the constants with temperature of the swelling medium as well as the activation energy of the swelling of the SAP can be determined. The data shows that at first, an increase in the hydrophobicity leads to a decrease of both the change rate of the swelling constant, as well as the activation energy to swell the microgels. This trend in both cases is broken as the hydrophobicity increases further for the crosslinker BBAA. Both results are visualized together in **Figure 10**.

As a result, we conclude that there are at least two separate influences of the crosslinkers hydrophobicity on the SAP microgel, which seem to have opposite effects on the swelling kinetics of the microgel and partially compete with one another. One influence of the crosslinker hydrophobicity was previously described

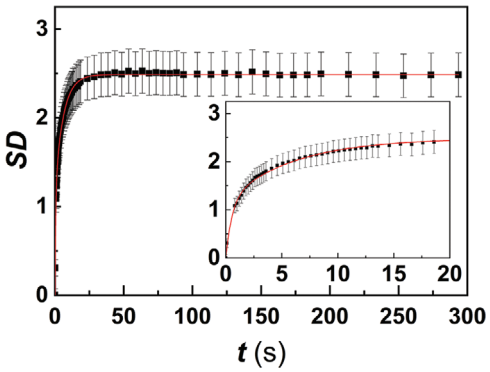

Figure 5. Swelling curve of a single superabsorbent polymer (SAP) microgel containing the crosslinker *N,N'*-methylenebisacrylamide (MBAA) in physiological saline solution at 45 °C. The error bars denote the possible error of the swelling degree (SD) calculated from the errors from the determination of the diameters of the particle at the start of the swelling and at time *t*. The red line is a fit to Equation (2). The inset shows a zoom onto the data between 0 and 20 s.

by Bromberg et al. The authors described that a higher hydrophobicity of co-monomers during the gel creation will lead to an increased degree of porosity of the gels.[11] Such an increased porosity of the microgel in our case would come from increasing *apparent* crosslink to crosslink distance, which may also be conceived as the distance between effective crosslinking nodes that actually consist of several locally close-by crosslinks. This kind of spatial inhomogeneity of the microgel crosslinking density can be expected to lead to a decrease in the activation energy needed for the swelling of the gel, as it facilitates solvent transport to and from the gel and is indeed observed for the crosslinkers MBAA to PBAA.

A competing effect of the hydrophobicity of the crosslinker might be the emergence of hydrophobic domains within the microgel, as detected in small-angle neutron scattering (SANS) experiments on poly (acrylic acid) microgels by Bromberg et al.[16] These hydrophobic domains might increase the activation energy of the swelling, as they need to be broken upon swelling. This effect should compete with the before-mentioned effect of increased porosity. Since the trends observed in both the change rates of the swelling constants as well as the activation energy reverse as the hydrophobicity of the crosslinker increases from PBAA to BBAA, we conclude that the effect of the hydrophobic domains in BBAA dominates over the increased porosity effect. Further support for this conclusion is given by the calculated reactivity ratios r_2 of the corresponding *N*-alkyleneacrylamides, for

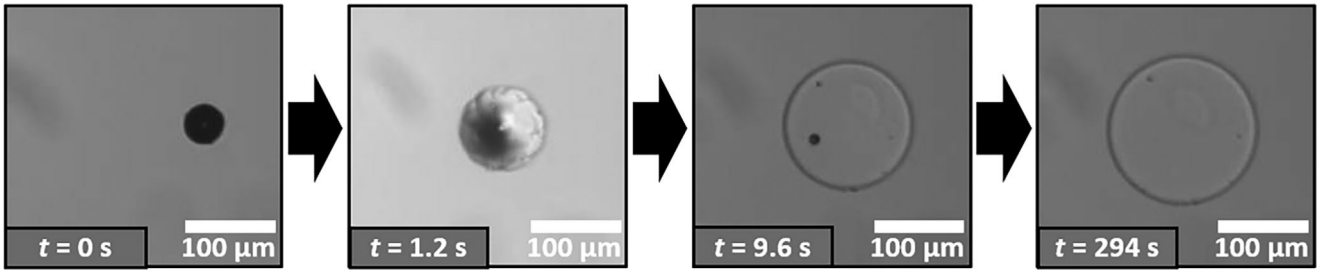

Figure 4. Extracted frames from the video of the swelling process of one of the microgels with typical length and timescales for reference.

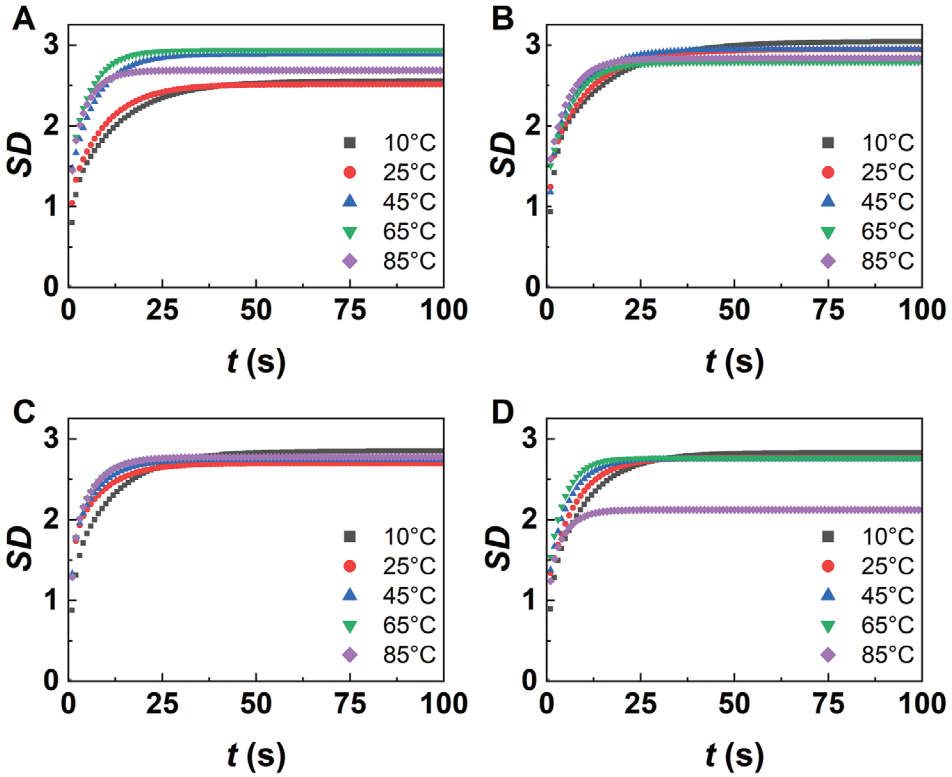

Figure 6. Fits of the swelling degree (SD) of the swelling data averaged over the particles of the superabsorbent polymer (SAP) microgel particles containing the different crosslinkers *N,N'*-methylenebisacrylamide (MBAA) (A), EBAA (B), PBAA (C) and BBAA (D) in physiological saline solution versus the time *t* spent in the swelling solution at temperatures of 10 °C, 25 °C, 45 °C, 65 °C, and 85 °C.

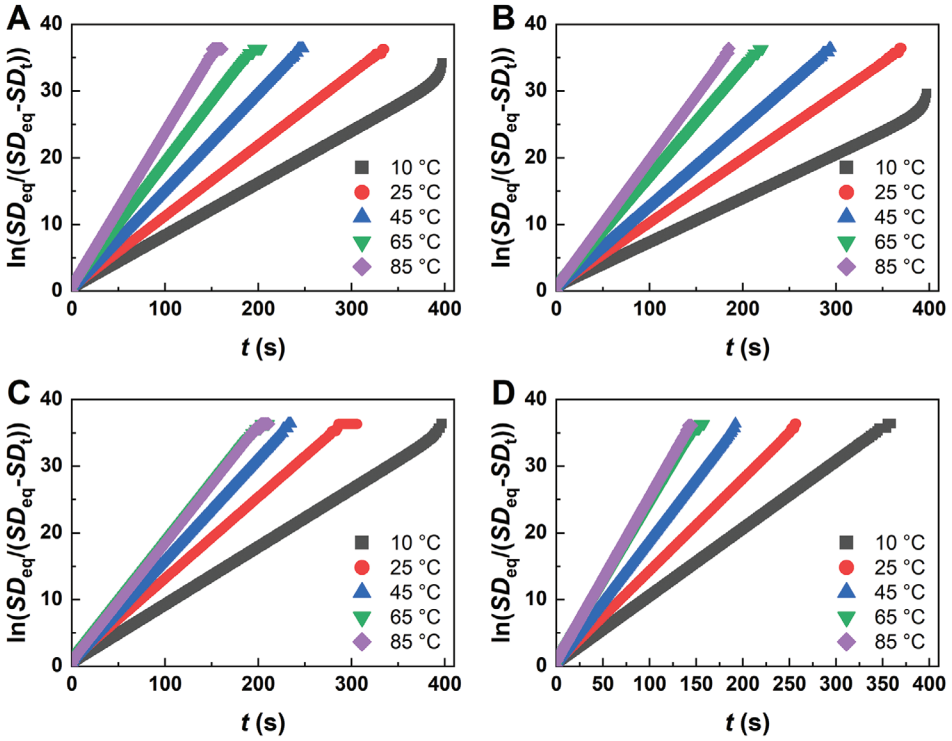

Figure 7. Plots of the natural logarithm of the swelling degree (SD) at equilibrium divided by the difference between the SD at equilibrium and the SD at time *t* versus the time *t* spent within physiological saline solution at different temperatures for the superabsorbent polymer (SAP) microgels containing the crosslinkers *N,N'*-methylenebisacrylamide (MBAA) (A), EBAA (B), PBAA (C), and BBAA(D).

Table 2. Calculated swelling constants k of the microparticles with the crosslinkers *N,N'*-methylenebisacrylamide (MBAA), EBAA, PBAA, and BBAA at the corresponding temperature of the swelling medium *T*.

T [°C]	k_{MBAA} [s^{-1}]	k_{EBAA} [s^{-1}]	k_{PBAA} [s^{-1}]	k_{BBAA} [s^{-1}]
10	0.079	0.067	0.087	0.101
25	0.107	0.096	0.121	0.138
45	0.146	0.121	0.152	0.184
65	0.183	0.164	0.175	0.235
85	0.231	0.191	0.175	0.247

Table 3. Calculated change rates of the swelling constant with temperature of the swelling medium versus the crosslinker used in the superabsorbent polymer (SAP) microgels.

Crosslinker	Δk [(s K)$^{-1}$]
MBAA	$2.00 \cdot 10^{-3}$
EBAA	$1.67 \cdot 10^{-3}$
PBAA	$1.59 \cdot 10^{-3}$
BBAA	$2.42 \cdot 10^{-3}$

which we found that with an increase of the hydrophobicity of the *N*-alkyleneacrylamides r_2 increases. Furthermore, in the case of *N*-butyleneacrylamide, the hydrophobicity of the co-polymer lead to a phase separation immediately after initiation. This finding is a strong indication that in the case of the crosslinker BBAA, a microphase separation happened during the gelation-process of the droplets, which can be associated to the formation of hydrophobic domains within the microgel.

Table 4. Activation energies of the microgel swelling, E_a, in relation to the corresponding crosslinker.

Crosslinker	E_a [kJ · mol^{-1}]
MBAA	11.9
EBAA	11.7
PBAA	10.0
BBAA	12.2

3. Conclusion

In this article, we systematically isolated the influence of the crosslinker hydrophobicity on the swelling kinetics of SAP microgels. We found two counteracting effects on the swelling kinetics resulting from an increase of the hydrophobicity of the crosslinker. The increase of the spatial crosslinking inhomogeneity of the microgels leads to a decrease of the activation energy of the swelling, which reverses at a further increase of the hydrophobicity of the crosslinker due to dominance of a second effect: the emergence of hydrophobic domains in the microgel. However, our research shows a narrow window in which an increase of the crosslinker hydrophobicity can have a positive effect especially for applications, in which fast swelling of dried hydrogel particles is desired.

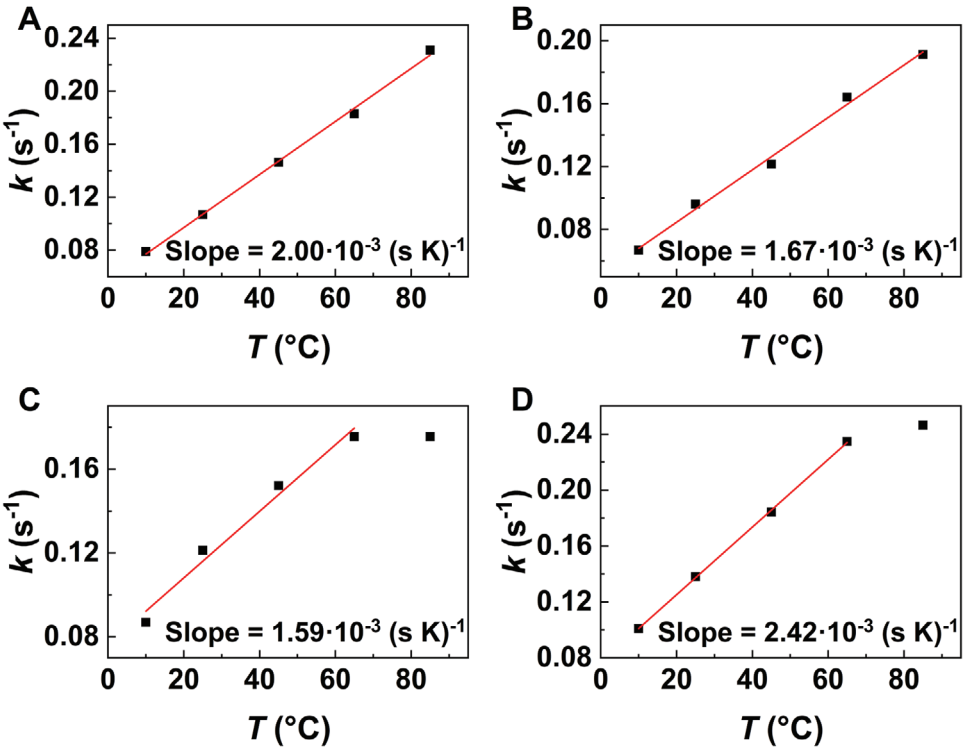

Figure 8. Swelling constant *k* of the superabsorbent polymer (SAP) microgels containing the crosslinkers *N,N'*-methylenebisacrylamide (MBAA) (A), EBAA (B), PBAA (C), and BBAA (D) versus temperature. The red lines are linear fits through the low temperature branch of the dataset.

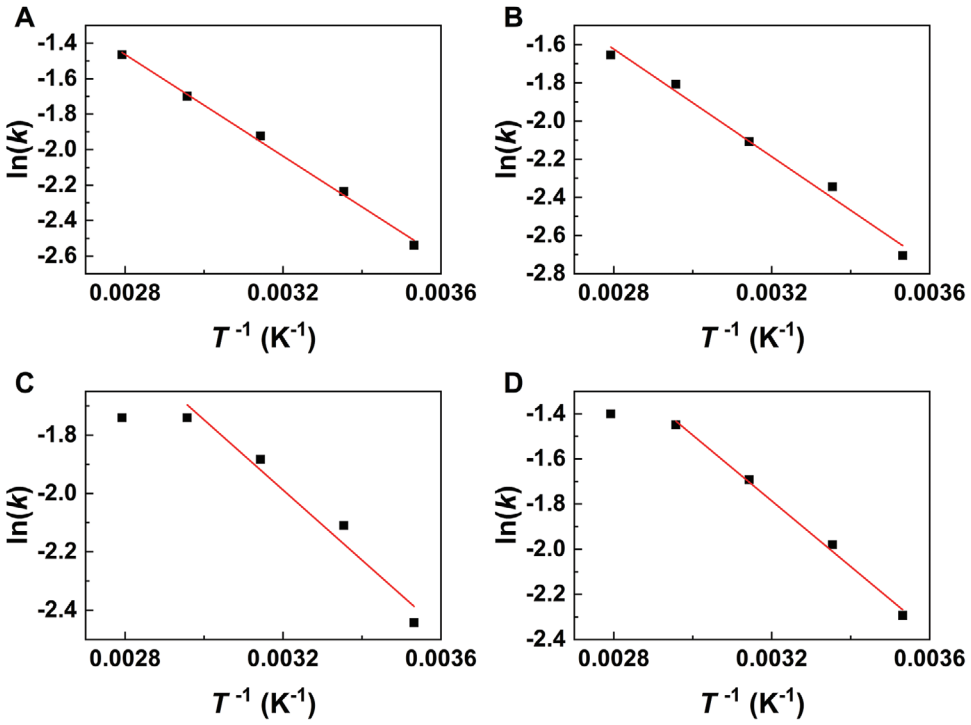

Figure 9. Arrhenius plots for the superabsorbent polymer (SAP) microparticles containing the crosslinkers *N,N'*-methylenebisacrylamide (MBAA) (A), EBAA (B), PBAA (C) and BBAA (D). The red line in each panel represents a linear fit, ignoring the plateau reached at high temperatures in the cases of (C) and (D).

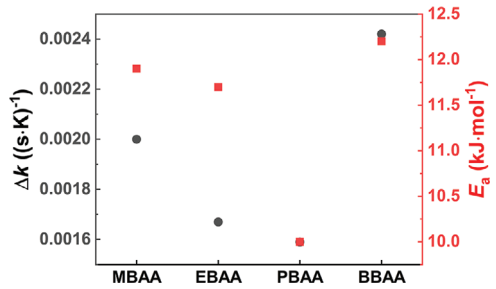

Figure 10. Calculated change rates of the swelling constants and activation energies of the microgel swelling for microgels containing the four different crosslinkers.

4. Experimental Section

Materials Used: Acrylic acid and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were purchased from Sigma-Aldrich, ammoniumperoxodisulfate (APS) from Acros Organics, sodium hydroxide solution 50% from Merck, MBAA, EBAA, PBAA, BBAA as well as *N*-methyleneacrylamide, *N*-ethyleneacrylamide, *N*-propyleneacrylamide, and *N*-butyleneacrylamide from BLDpharm. For the continuous phase in the microfluidic experiments low viscosity paraffin oil from Roth was used with ABIL EM 90 as surfactant from Evonik Industries. All chemicals were used as received.

SAP Microparticle Synthesis via Droplet-Based Microfluidics: For the droplet-based microfluid experiments an aqueous solution (dispersed phase) of 50% neutralized acrylic acid was prepared by adding 0.56 g of a sodium hydroxide solution (50%) (7 mmol) dropwise to 1.00 g of acrylic acid (14 mmol) diluted with 3.43 mL of milli-Q water. To the solution 0.3 mol% crosslinker (versus acrylic acid) was added, and the mixture was shaken (250 rpm) over night for the crosslinker to dissolve. Once a clear solution was obtained 5 mg of APS initiator was added (dispersed phase). For the continuous phase low viscosity paraffin oil was mixed with 10 wt% of ABIL EM90 as surfactant. An amount of 2 g of TEMED was added to 5 mL of the continuous phase (as APS initiation activator), and 0.5 mL of the continuous phase solution was filled into the collection vial used during the microfluidic experiment. After about 8 mL had been collected, the collection vial was changed with a fresh vial containing fresh 0.5 mL of TEMED mixed continuous phase.

Both the dispersed phase as well as the continuous phase were filled in syringes and pumped into a self-made polydimethylsiloxane (PDMS) microfluidic chip using two PHD ULTRA syringe pumps from Harvard Apparatus. The flowrates were adjusted for optimal droplet creation with the dispersed phase having flowrates between 75 and 125 µL h^{-1} and the continuous phase 700 and 725 µL h^{-1}, and the experiment was left running for up to 24 h. The droplets were left for a further 24 h at room temperature to ensure complete polymerization. Afterwards, the continuous phase was removed, isopropanol was added, and the microgels were washed five times with 5 mL of isopropanol each, followed by further five times washing with acetone. Afterwards the microgels were dried using a hotplate at 90 °C for 2.5 h to conduct for the swelling kinetic studies. The dried microgels had a size between 50 and 60 µm.

Copolymer Synthesis for Determination of the Reactivity Ratios of the Co-Monomers: Acrylic acid was first diluted with 20 mL milli-Q water and then neutralized with sodium hydroxide solution. The corresponding amount of *N*-alkylacrylamides was added and the mixture was bubbled for 3 h with argon. An amount of 0.11 g of APS was dissolved in 0.5 mL of milli-Q water, and 75 µL TEMED was added to initiate the polymerization. The progress of the polymerization was checked every 10 min by trying to precipitate aliquot samples in excess oxolane. Once a noticeable precipitation was observed the reaction was terminated in oxolane, whereby the polymer precipitated. The product was isolated by filtration, re-dissolved in water, dialyzed for 1 week against deionized water, and finally gained

in solid form by freeze drying. For analysis of the copolymer composition, 3 mg was dissolved in D_2O and subjected to the ^{1}H-NMR-experiments conducted on an NMR spectrometer of type Bucker AC 400 (400 MHz). The resulting spectra were evaluated using the software MestReNova V5 by MESTRELAB RESEARCH S.L.

Swelling Experiments of the SAP Microparticles: A small amount of the microgel particles was filled into a single well of a µ-Slide 8 Well ibiTreat made by Ibidi and separated until single free lying microgels could be seen under an inverted microscope (Axio Vert.A1 from Zeiss). Using a camera UI-3060CP from IDS and the program uEye Cockpit, a video of the microgel swelling was recorded. As swelling medium, a physiological salt solution (9 g L^{-1} of sodium chloride in deionized water with pH 5) was prepared and heated to the corresponding temperature using a thermostat CF31Kryo-Kompakt-Thermostat from Julabo. Once the temperature was reached, the swelling solution was left for 1 h at the temperature being lightly shaken. After that, 1 ml of the swelling solution was then added to the microparticles as the video recording was already running, and the swelling of the spheres was captured for 5 min. The resulting video was then cut into single frames using a self-written python routine, which is available in the Supporting Information, and the single frames analyzed using the free software image-J. The particles area was determined, and from the area the corresponding diameter of the particles was calculated at various times during the swelling.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

crosslinker hydrophobicity, superabsorbent polymers, swelling kinetics

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