# Characterization of polyacrylamide gels for use as a heat and cold storage material

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## Preface

This report concludes the author's graduation project at the Faculty of Chemical Engineering and Materials Science. The work has been done as a part of the Materials Science curriculum, and has been supervised by Prof. dr. ir. J. van Turnhout of the Department of Polymer Science and Technology.

The original goal of this project was to gain more insight in the suitability of hydrogels as heat or cold storage material. Although they are known from patent literature, hardly any scientific publications on this topic can be found. In this report the results of an orientational study on the application of hydrogels as a heat or cold storage material are provided. A survey of factors that play an important role in this application is given, and I hope it will prove a good starting point for further work in this field.

In the course of this project, I grew acquainted with different analysis methods, each involving the use of specialized equipment. I would like to take this opportunity to express my gratitude towards all staff members of the polymer group who were willing to share their time and expertise to introduce me to their specialist fields, and help me performing my measurements. Of course I am also grateful to those people of the other departments of this faculty and from TNO who were willing to let me use their equipment and assisted me with the synthesis of my samples.

Also I would like to thank Prof. v. Turnhout, especially for reading my many draft reports and for his valuable comments on my written English. Furthermore, I am much obliged to the colleagues with whom I worked daily: fellow-students, Ph.D. students, post-docs and technical and scientific staff of the polymer group. Sincere thanks for your friendly support, coffee, discussions and encouragement over the past few months. I could not have finished this work without you.

Finally, I would like to thank Peter, my family, friends and flatmates for their patience, understanding and for cheering me up when I needed it.

Marjan Schippers Delft, November 1997

#### Summary

Polyacrylamide gels with different crosslink densities were studied for the application as a heat storage material. At polymerization the gels contained about 10% polymer and 90% water. Some of the gels showed phase separation and were clouded. The turbidity of the gels increased with crosslink density.

The equilibrium shear moduli of the polyacrylamide gels were determined to verify whether the network formation was successful. The storage modulus was found to increase with increasing amount of crosslinker added which indicates that indeed networks with increasing crosslink density had been formed.

The swelling of the polyacrylamide gels in water, and aqueous solutions with different salt concentrations was determined. The swelling of the gels was found to increase with decreasing crosslink density. The swelling of the (uncharged) polyacrylamide gels did not depend on the salt concentration of the solutions and was comparable to the swelling in demineralized water. This implies that no significant hydrolysis has taken place.

The thermal properties of the gels were studied by means of inverse photopyroelectric analysis and the Isomet method. The thermal effusivities obtained by both the Isomet method and the inverse photopyroelectric analysis agreed with each other, but the accuracy of the methods must be improved to be able to elucidate the effect of the crosslink density.

Differential scanning calorimetry was performed to study the freezing behaviour of the gels. The swollen gels (containing  $\leq 10 \text{ mass}\%$  polymer) showed higher glass transition temperatures than the unswollen ones (containing 10 mass% polymer). The glass transition temperatures were all below 0°C and increased with crosslink density. From the thermograms also the amount of frozen water in the gels was calculated.

Furthermore, thermogravimetric analysis has been done on the polyacrylamide gels and on pure water. The drying rate was found to decrease by the presence of the polymer. However, the relationship between the drying rate and the crosslink density is unclear.

## List of symbols

а	[-]	Activity
$C_p$	[J/kgK]	Specific heat capacity (Sometimes given in J/m <sup>3</sup> /K)
С	[M]	Concentration
d	[m]	Thickness
f	[Hz]	Frequency
G	[Pa]	Shear modulus
ΔG	[J/mole]	Gibb's free energy
Η	[-]	Water fraction
ΔH	[J/mole]	Enthalpy
I	[A]	Current
Ι	[mole/m <sup>3</sup> ]	Ionic strength
i	[-]	Degree of ionization
Κ	[-]	Dissociation constant
L	[m]	Thickness
M,	[kg/mole]	Molecular weight of crosslinker
m	[kg]	Mass
0	[1]	Heat of transition
R	8.3143 J/moleK	Gas constant
Р	[mass %]	Polymer concentration
Т	[K] or [°C]	Temperature
V	[m <sup>3</sup> ]	Volume
v.	[mole/m <sup>3</sup> ]	Concentration of active chains
V.,	[m <sup>3</sup> /mole]	Molar volume of the structural unit of the polymer
V.	[m <sup>3</sup> /mole]	Molar volume of the swelling agent
X	[mole%]	Extent of crosslinking
Z	[-]	Charge
		en ge
α	$[m^2/s]$	Thermal diffusivity ( $\alpha = \lambda/\rho C_{r}$ )
γ	[-]	Shear strain
η	[J/m <sup>2</sup> Ks <sup>1/2</sup> ]	Thermal effusivity or heat penetration coefficient $(n = \sqrt{\lambda_0 C})$
λ	[W/mK]	Thermal conductivity
μ	[mole/m <sup>3</sup> ]	Concentration of crosslinks
μ	[1]	Chemical potential
$\nu^+, \nu$	ν,ν [-]	Stoichiometric coefficients
ξ	[-]	Volume fraction
ρ	$[kg/m^3]$	Density
τ.	[Pa]	Shear stress
$\Phi$	[-]	Functionality of crosslinks
$\phi$	[m]	Diameter
x	[-]	Flory interaction parameter
ω	[-]	Mass fraction

## Abbreviations

AAm	Acrylamide
AMPS	Ammonium persulfate
DVB	Divinylbenzene
NNMBA	N,N'-Methylenebisacrylamide
PVDF	Poly(vinylidene fluoride)
SMB	Sodium metabisulfate
TEGDA	Tetraethyleneglycoldiacrylate
TEGDMA	Triethyleneglycoldimethacrylate
TEMED	N, N, N', N'-Tetramethylethylenediamine

DSC	Differential scanning calorimetry	
IPPE	Inverse photopyroelectric analysis	
TGA	Thermogravimetric analysis	

## 1 Introduction

Superabsorbing polymers, like the polyacrylamide used for this research project, are polymer networks, which can absorb large amounts of fluid. The fluid absorbed is usually water or an electrolyte. The behaviour of these materials, also called gels or hydrogels, is somewhere in between that of solids and liquids. They exhibit the cohesive properties of a solid and the diffusive transport properties of a liquid. However, different definitions of gels can be found in literature [1]. The polymer network can be formed by physical or chemical crosslinking. The polyacrylamide gels used in this project are an example of chemically crosslinked networks. The amount of fluid contained by the gel is dependent on conditions such as temperature, solvent composition (presence of ionic species and acidity), application of an electrical field and degree of crosslinking.

The typical behaviour of gels makes them suitable for a wide variety of applications. A wellknown application is of course in baby diapers, but they can also be employed in artificial muscles, contact lenses and food packaging. Gels which are sensitive to temperature or pH are employed in drug delivery systems and in separation or concentration methods for aqueous solutions of large biomolecules like proteins and enzymes. Agricultural purposes may be found in the retainment of water and solutes, for example fertilizers, in dry areas.

The aim of this research project is to characterize polyacrylamide gels for use as a heat and cold storage material. The most familiar way to store heat is the conventional hot-water bottle. Since water has a large specific heat capacity it is suitable for storing heat, but it exhibits one major disadvantage, namely the possibility of leakage. Gels are expected to be a good alternative, since they do not flow and consist mainly of water, so that the problem of leakage can be overcome while the ability of heat storage will hardly be affected. Furthermore, gels have the (commercial) advantage that they can be given any shape and can be heated in a microwave oven.

For this project polyacrylamide was chosen. Other superabsorbing polymers are for instance polyacrylate, polyacrylic acid, polymethacrylic acid, polyvinylalcohol and polyhydroxymethylene. Polyacrylamide is well-known from literature and easy to prepare. In this study polyacrylamide gels were prepared with different crosslink densities. One might expect that the crosslink density of the gel has an important influence on its properties. First, the swelling behaviour of the gels was studied. The water absorption capability of the gels is expected to depend on the crosslink density. When less polymer is necessary to retain the same amount of water, the cost of future products will be reduced. Rheological experiments have been performed to characterize the network formed by free radical polymerization. The thermal properties of the gel were determined by inverse photopyroelectric analysis. When gels are to be used as heat (or cold) storage materials, it is necessary to acquire some information about their thermal properties. The specific heat capacity and thermal conductivity give insight in the efficiency of the gel as a heat storage material. Differential scanning calorimetry has been performed to study the freezing behaviour of the gels. This technique

can be used to reveal information on the states of water present in the gel. Thermogravimetric analysis was performed to study the water-retention of the gels at high temperatures. Finally the microwave heating times were determined. This is interesting for the application as "hot-water bottle", since this is a quick and easy way to heat the material.

Some theoretical aspects, among other things the effect of synthesis conditions on the gel properties and the equilibrium swelling theory, are dealt with in chapter 2. The experiments are described in chapter 3. The results are presented and discussed in chapter 4. The conclusions can be found in chapter 5 and finally in chapter 6 some suggestions for further research are given. For those who are interested in the subject, more material on superabsorbent polymers can be found in references [2-8].



Figure 2.1: Molecular structure of a polyacrylamide network [14].



Figure 2.2: Forming of a polyacrylamide network: 1) activation of TEMED by AMPS, 2) combination with acrylamide and shift of active site to free end, 3) incorporation of bisacrylamide crosslinker [10].

## 2 Relevant topics in literature on polyacrylamide gels

## 2.1 Synthesis of polyacrylamide gels

Polyacrylamide gels are usually prepared in aqueous solution by free radical polymerization. The molecular structure of polyacrylamide is presented in figure 2.1. Most researchers use N,N,N',N'-tetramethylethylenediamine as an accelerator and ammonium persulfate for the initiation of the reaction between the acrylamide monomer and the N,N'-methylenebis-acrylamide crosslinker [9-14]. First, ammonium persulfate reacts with N,N,N',N'-tetramethylethylenediamine, resulting in a N,N,N',N'-tetramethylethylenediamine radical. To this activated molecule, acrylamide or bisacrylamide monomers may be attached. Figure 2.2 shows the polymerization and crosslinking process of polyacrylamide [10]. Sometimes only ammonium persulfate is used without N,N,N',N'-tetramethylethylenediamine [15] or sodium metabisulfite is used as an accelerator instead of N,N,N',N'-tetramethylethylenediamine [16-17].

The properties of the gel, such as the equilibrium swelling degree, shear modulus, effective crosslink density and turbidity depend on the synthesis conditions. The turbidity of the gel and heterogeneity of the microstructure are determined by the temperature during synthesis. The temperature depends on the concentration and type of initiator and accelerator used. Gehrke et al. [16] studied this effect. In figure 2.3, the reaction temperature is given for different initiator/accelerator combinations and concentrations. These poly(N-isopropylacrylamide) gels were also prepared in different moulds to study the effect of mould geometry. Of course, the temperature will depend on the mould geometry since heat is transferred more easily from a mould with a larger surface/volume ratio. The rapid temperature rise observed in this figure is due to the Trommsdorf effect, which means that the viscosity of the solution increases rapidly near the gel point and the polymer/solvent compatibility decreases with increased conversion and temperature. This causes a reduction in the termination rates of the growing chains and since the polymerization reaction is highly exothermic, the temperature will rise even more. Gehrke et al. [16] also prepared gels at a temperature of 0°C. They found that gels containing 10% monomer and crosslinker in the pregel solution, with a crosslink ratio of 1.88 mole% were transparent when prepared at 0°C and opaque when prepared at ambient temperature. The swelling degree of these gels increased with initiator concentration, but the dependency on the reaction temperature was stronger.

Other variables which affect the properties of the gel are the monomer and crosslinker concentrations in the pregel solution, the extent of reaction, oxygen concentration and reagent purity. The gels are characterized by the extent of crosslinking and the polymer concentration. The degree of crosslinking is expressed in mole% crosslinker added:

$$mole\%X = \frac{NNMBA \ (moles)}{AAm \ (moles) + \ NNMBA \ (moles)} * 100\%$$
(2.1)

The polymer (mass) concentration in the gel, %P, is calculated by:

$$\%P = \frac{AAm (g) + NNMBA (g)}{reaction \ mixture \ (g)} * 100\%$$
(2.2)

The reaction mixture is a solution of acrylamide, N,N'-methylenebisacrylamide, N,N,N',N'tetramethylethylenediamine and ammonium persulfate in water.

The crosslink density influences the photopermeability characteristics of the gels. Chandy and Rajasekharan Pillai [15] studied this effect in 10 %P gels. The gels characterized by 5 and 10 mole% crosslinker were transparent and the ones with 15 and 20 mole% crosslinker were opaque or white. Chandy and Rajasekharan Pillai attribute this to the heterogeneous nature of the polymer. With a larger amount of crosslinker present in the reaction mixture the main chain movements during synthesis will be greater, resulting in an increased heterogeneity in the crosslink distribution. Chandy and Rajasekharan Pillai assume that the absorbed water will form clusters in the gel. When less crosslinking agent is used, the crosslinks will be distributed uniformly and therefore also the water will be distributed more uniformly throughout the network. A more detailed study on the turbidity of gels can be found in the article of Sedláček and Koňák [18]. They studied the influence of temperature changes on the turbidity of poly(2-hydroxyethylmethacrylate) with spectrophotometry.

## 2.2 Hydrolysis of polyacrylamide

When polyacrylamide gels are prepared as described in the previous section, an uncharged polymer network is obtained. These are studied in this project. Nevertheless, it is possible to modify this network into a charged network by converting some of the aminocarbonyl groups (-CONH<sub>2</sub>) into carboxyl (-COOH) groups [10,19,20].

$$-CONH_2 + H_2O \rightarrow -COOH + NH_3 \tag{2.3}$$

This process is called hydrolysis. In figure 2.4, a schematic presentation of the hydrolysis process is given. The carboxyl groups function as an organic acid and some of the groups will ionize, resulting in a negatively charged network. The degree of hydrolysis affects the swelling behaviour of the gels, as can be seen in figure 2.5. The swelling of the gel in this figure is given as a ratio of the swollen gel volume to the initial gel volume. The swelling agent in this case was an acetone-water mixture instead of just water. Since water (polar) is a better solvent for an ionomeric gel than acetone, the swelling increases with decreasing acetone concentration. The effect becomes stronger when more hydrolyzed groups are present.



Figure 2.3: Reaction temperature in 11.2 mm glass tubes: ▲ 50mg AMPS/25mg TEMED, ○ 3mg AMPS/1.5mg TEMED, ● 3mg AMPS/2.5mg SMB; in 14.1mm tubes: □ 3mg AMPS/1.5mg TEMED, ■ 3mg AMPS/2.5mg SMB [16].



Figure 2.4: Hydrolysis of polyacrylamide [10].

The hydrolysis of the aminocarbonyl groups depends on the temperature, acidity and time. The latter is already observed in figure 2.5. Muller [21] studied the influence of temperature and acidity. The degree of hydrolysis is found to increase with temperature and acidity, see figures 2.6 and 2.7. According to Ohmine and Tanaka [20] and Moens and Smets [22] hydrolysis can also take place in alkaline solutions (pH exceeding 12). A more elaborate treatise of this topic can be found in references [23-26]. From figures 2.6 and 2.7 it can be seen that the degree of hydrolysis increases with temperature. The effect of increasing hydrolysis at higher temperatures can be very important when gels are to be used as a heat storage material. However, if the swelling capacity is increased, this is not necessarily a disadvantage. The exact reason why charged gels show more swelling than uncharged gels in water or aqueous electrolyte solutions is explained in section 2.6, where a short outline of the equilibrium swelling theory is given.

## 2.3 Modulus and network properties

According to the rubber elasticity theory given by Flory [27], the relation between shear stress  $\tau_s$  and shear strain  $\gamma$  is:

$$\tau_s = RT \nu_e \gamma \tag{2.4}$$

Here,  $v_e$  denotes the concentration of elastically active chains (the chains that contribute to the elasticity of the network), R is the gas constant and T the temperature. The rubber elasticity theory assumes affine deformation of the network, which means that macroscopic deformations lead to deformations of the network chains in the same ratio as the bulk. Furthermore it was presumed that the volume remained constant throughout deformation. The relation between the network structure and the shear modulus G is thus:

$$G = v_e RT$$
 (2.5)

When all chains end at crosslinks and the crosslinks have a functionality  $\Phi$  then v<sub>e</sub> can be replaced by  $\mu \Phi/2$ :

$$G = \frac{\Phi}{2} \mu RT \tag{2.6}$$

where  $\mu$  is the concentration of crosslinks. This concentration can be calculated from the composition of the reaction mixture, leading to:

$$G = \frac{\Phi}{2} \frac{\omega_J}{M_J} \rho RT \tag{2.7}$$

The symbol  $\omega_1$  denotes the mass fraction of crosslinker in the system,  $M_1$  the molar mass of the crosslinker and  $\rho$  the density of the gel. A more in depth treatise of the subject can be



Figure 2.5: Influence of hydrolysis time in days on equilibrium swelling of polyacrylamide gels in acetone-water mixtures [19].



Figure 2.6: Hydrolysis of polyacrylamide at 60°C and different pH-values. The hydrolysis at start was 31% [21].

found in references [27-30]. Some values of the modulus obtained experimentally by others are given in table 2.1 [12-13,31].

## 2.4 Water in hydrogels

Water absorbed by a hydrogel can be present in three different states, bound, free and intermediate or interfacial water [32-38]. Higuchi and Iijima [34] define free water as water having the same phase transition temperature as bulk water. This water shows no interaction with the polymer chains. On the other hand, in the case of bound water the interactions with the polymer are very strong and this water shows no detectable phase transition in the temperature range 200-273 K. Interfacial water shows weak interactions with the polymer. This water behaves partially like free water and partially like bound water. This "freezable" bound water has a phase transition temperature lower than 273 K. There are several ways to determine the amount of water present in either the bound or free state [39]. These are for instance differential scanning calorimetry (DSC) [15,34-35,37,40], dilatometry [35,40], nuclear magnetic resonance spectroscopy (NMR) [13,41] and dielectric relaxation [40]. However, different measurement techniques may probe different physical phenomena and therefore the values found for the fraction of bound water may differ. Additionally, there is no sharp boundary between bound and free water, which may also lead to different values [39].

Higuchi and Iijima [34] performed differential scanning calorimetry on poly (vinyl alcohol) gels (PVA) during heating and cooling at a rate of 10 K/min. The results can be found in figures 2.9 and 2.10. They observed two peaks, which overlapped at higher water content. When the amount of water is decreased the two peaks become separated. The sharp peak at 273 K is the one of free water and the broad peak is due to freezable bound water (intermediate water). When the total amount of water is increased this peak shifts towards 273 K. In the cooling curves, two crystallization peaks are observed, one at 255 K and another at 230 K. In their article, Higuchi and Iijima show that for gels containing less water, the water for the first peak (255 K) in the cooling curve contributes to both the first and second peak in the heating curve, while the water for the second peak in the cooling curve contributes solely to the second peak in the heating curve. The broad peak is due to the existence of water phases which crystallize with different rates of nucleation.

From the thermograms obtained by DSC, the amount of unfrozen water has been determined as a function of the water fraction in the gel, see figure 2.18. The amount of frozen water was calculated using the melting enthalpy of pure ice or crystallization enthalpy of pure water.

$$m^{h} = \sum_{n} \frac{Q_{n}^{h}}{\Delta H_{n}^{h}}$$
(2.8)



Figure 2.7: Hydrolysis of polyacrylamide at 90°C and different pH-values. The hydrolysis at start was 31% [21].

Table 2.1: Shear moduli of polyacrylamide gels found in literature [12,13,31]. Rodin [13] determined elastic moduli, these are marked with an asterisk.

Mass% polymer	Mole% crosslinker	Modulus (kPa)
10.1	0.5	5.9*
10.1	1.0	11.2*
12	2.5	11.8
12	3.5	12.9
12	5.0	13.7
10	0.7	3.43

$$m^{c} = -\sum_{n} \frac{Q_{n}^{c}}{\Delta H_{n}^{c}}$$
(2.9)

In these equations, m denotes the mass of freezable water, Q the transition heats obtained experimentally and  $\Delta H$  the enthalpy for phase transition. The superscripts h and c refer to the heating and cooling process respectively and the subscript n to the state of the water. The unfrozen water,  $m_u$ , content can now be calculated by subtracting the freezable water from the total water content,  $m_t$ . This method has been applied by most researchers [15,36,37].

However, for supercooled bulk water the crystallization enthalpy is lower than that of bulk water at 273 K [42]. Higuchi and Iijima made a correction for this in their calculations. The crystallization enthalpy of supercooled bulk water,  $\Delta H_T$  can be expressed as:

$$\Delta H_{T} = \Delta H_{273} - \int_{T}^{273} \Delta C_{p} dT$$
 (2.10)

Here,  $\Delta H_{273}$  is the crystallization enthalpy of bulk water at 273 K and  $\Delta C_p$  the difference in heat capacities of ice and supercooled water. They applied a similar equation for intermediate water.

Chandy and Rajasekharan Pillai [15] performed DSC measurements to characterize the water in polyacrylamide gels. In figure 2.11, the frozen water content is given as a function of the crosslink density in mole percent. They did not correct their results for the difference in the heat capacities of ice and supercooled water.

The bound water content can also be determined by thermogravimetric analysis [39,43]. According to this method bound water is the moisture content at the boundary of the constant-rate weight loss period and falling rate weight loss period. Ayer [43] examined the drying rate of wood fibers. The (adiabatic) drying process took place in a conditioned atmosphere at 105°C. An example of the drying curves obtained in this way is given in figure 2.8. Ayer observed three drying periods, one with a constant drying rate and two falling-rate periods. The first, constant drying rate period is ascribed to the evaporation of unbound (or free) water from the surface of the fibers. During the first falling-rate period capillary or imbibed water is released. During the second falling-rate period the drying rate decreases rapidly. Ayer refers to this kind of water as "primary absorbed" water.



Figure 2.8: Drying rate of wood pulp in grams/min. vs. mass% fiber [43].



Figure 2.9: D.S.C. heating curves of water-swollen PVA films for different water mass fractions (H); heating rate 10 K/min. [34].

#### 2.5 Thermal properties

The thermophysical properties of polyacrylamide gels, such as the specific heat capacity and thermal conductivity were determined by Hirata *et al.* [44]. They considered the gel to be a two-component system of water and polyacrylamide and developed a model for the thermophysical properties of the gel. In order to test the model Hirata *et al.* measured the thermal properties of the gel and by taking the properties of water in the gel equal to those of pure water, they calculated the properties of polyacrylamide in the gel. These values were compared with those of other (dry) polymers. The amounts of initiator and accelerator were small enough to be neglected. The gels used for these experiments were characterized by a crosslink density of 3 mass% X ( $\approx 1.5$  mole%) and contained 10, 20, 30 and 40 % polymer.

When the gel is assumed to be a two-component system the total gel volume V is equal to the sum of the volumes of the water  $(V_w)$  and polyacrylamide  $(V_p)$  phases:

$$V = V_{w} + V_{p} \tag{2.11}$$

The mass m of the gel is:

$$m = m_{w} + m_{p} \tag{2.12}$$

where  $m_w$  is the mass of the water phase and  $m_p$  the mass of the polymer phase. The volume fraction  $\xi$  and the mass fraction  $\omega$  of the polyacrylamide in the gel can be expressed as:

$$\xi = \frac{V_p}{V} = \frac{\rho_p}{\rho_p^*} \tag{2.13}$$

$$\omega = \frac{m_p}{m_w + m_p} = \frac{\rho_p}{\rho_p + \rho_w^* (1 - \rho_p / \rho_p^*)}$$
(2.14)

where  $\rho_p^* = m_p/V_p$  the density of polyacrylamide,  $\rho_w^* = m_w/V_w$  the density of water and  $\rho_p$  (=m/V) can be calculated from the polymer concentration (%P) in the gel, see also equation (2.2). The model is compared with the experimental results in figure 2.12. For the density of the gel  $\rho$  the following relation can now be derived from (2.11) and (2.12):

$$\frac{1}{\rho} = \frac{1}{\rho_{w}^{*}} (1 - \omega) + \frac{1}{\rho_{p}^{*}} \omega$$
(2.15)

$$\rho = \rho_w^* (1 - \xi) + \rho_p^* \xi \tag{2.16}$$



Figure 2.10: D.S.C. cooling curves of water-swollen PVA films for different water mass fraction (H); cooling rate 10 K/min. [34].



Figure 2.11: Dependence of the frozen water content of polyacrylamide gels on the degree of crosslinking [15].

Hirata [44] expressed the gel density  $\rho$  as follows:

$$\frac{1}{\rho} = \frac{1}{\rho_w^*} - \left(\frac{1}{\rho_w^*} - \frac{1}{\rho_p^*}\right) \frac{\rho_p}{\rho}$$
(2.17)

The specific heat capacity of the gel is found to decrease with increasing polymer concentration (%P), while the temperature dependence increases with %P, see figure 2.13. For the specific heat capacity,  $C_p$ , of the gel, Hirata *et al.* [44] derived the following relationship:

$$C_{p} = \omega C_{p_{\star}}^{\star} + (1 - \omega) C_{p_{\star}}^{\star}$$
(2.18)

Here,  $C_{p,p}^{*}$  is the specific heat capacity of the polymer and  $C_{p,w}^{*}$  the specific heat capacity of water. The relation between the specific heat capacity of the gel and the mass fraction of the polymer in the gel is given in figure 2.14. The specific heat capacity of water in the gel is equal to that of free water.

The dependence of the thermal conductivity of the gels on the temperature and polymer concentration is given in figure 2.15. The structure of polyacrylamide gels is a rather complicated three-dimensional network structure. Hirata *et al.* [44] made an attempt to estimate the effect of concentration on the thermal conductivity. Two approaches were examined for this purpose: a multiple layer model with layers aligned parallel to the direction of heat transfer and one with the layers perpendicular to this direction, see figure 2.16. In the case of the parallel model, the thermal conductivity  $\lambda$  of the gel is given by:

$$\lambda = \xi \lambda_p^* + (1 - \xi) \lambda_w^* \tag{2.19}$$

where  $\lambda_{p}^{*}$  and  $\lambda_{w}^{*}$  are the thermal conductivities of polyacrylamide and water respectively. For the model with the multiple layers aligned perpendicular to the direction of heat flow the thermal conductivity can be described by:

$$\frac{1}{\lambda} = \frac{\xi}{\lambda_p^*} + \frac{1-\xi}{\lambda_w^*}$$
(2.20)

The results for the latter model are given in figure 2.17. The parallel model gave negative values for  $\lambda_p^*$ , which have no physical meaning. Thus, it seems that the heat transfer through the gel is governed mainly by the thermal resistances of water and the polymer network perpendicular to the heat flow direction.



Figure 2.12: Density of polyacrylamide gels according to Hirata's model [44].



Figure 2.13: Specific heat capacity of polyacrylamide gels containing 10, 20, 30 and 40% polymer vs. temperature [44].

#### 2.6 Swelling of polyacrylamide gels

When a charged network is placed in a swelling agent, three contributions to the free energy  $\Delta G$  of the system can be distinguished [10,45,46]. These are mixing,  $\Delta G_{mix}$ , elastic-retractive,  $\Delta G_{el}$ , and ionic free energies,  $\Delta G_{ion}$ :

$$\Delta G = \Delta G_{mix} + \Delta G_{el} + \Delta G_{ion} \tag{2.21}$$

This is the most general case. In this project uncharged networks were studied for which  $\Delta G_{ion} = 0$ . Equation (2.21) can be written in terms of chemical potentials by taking the derivative of each term in equation (2.21) with respect to the number of molecules of swelling agent in the system.

$$\mu_{1} - \mu_{1}^{0} = (\Delta \mu_{1})_{mix} + (\Delta \mu_{1})_{el} + (\Delta \mu_{1})_{ion}$$
(2.22)

Here,  $\mu_1$  denotes the chemical potential of the swelling agent in the polymer-swelling agent mixture and  $\mu_1^0$  is the chemical potential of the pure swelling agent. At equilibrium, the chemical potential of the swelling agent,  $\mu_1$ , equals that of the swelling agent in the solution surrounding the polymer,  $\mu_1^*$  and equation (2.22) becomes:

$$(\Delta \mu_1^*)_{ion} - (\Delta \mu_1)_{ion} = (\Delta \mu_1)_{mix} + (\Delta \mu_1)_{el}$$
(2.23)

The left-hand side of this expression represents the difference between the ionic contributions from the chemical potentials inside and outside the gel. The right-hand side signifies the sum of the contributions to the chemical potential of the mixing and elastic forces due to polymer-swelling agent interactions.

The mixing contribution is due to the interactions between the polymer and the solvent, which can be repulsive or attractive depending on the electrical properties. If the interaction is attractive, the total energy is lowered if the polymer molecules are surrounded by solvent molecules. Repulsive interaction leads to exclusion of the solvent molecules. This contribution to the free energy of the system is temperature independent, but it does respond to changes in solvent composition. The mixing contribution is given by:

$$(\Delta \mu_1)_{mix} = RT \left[ \ln(1 - \xi_{2,s}) + \xi_{2,s} + \chi_1(\xi_{2,s})^2 \right]$$
(2.24)

where R is the gas constant, T the temperature,  $\chi_1$  the Flory interaction parameter and  $\xi_{2,s}$  the polymer volume fraction at swelling equilibrium. Subscripts 1 and 2 refer to swelling agent and polymer, respectively [10,27,45,47].

(0.00)



Figure 2.14: Specific heat capacity of polyacrylamide gel according to Hirata's model [44].



Figure 2.15: Thermal conductivity of polyacrylamide gels containing 10, 20, 30 and 40% polymer vs. temperature [44].

The elastic contribution can both stimulate and hinder the swelling of the gel, depending on the conditions of the polymer chains (extended or contracted), the magnitude of this force is temperature dependent. The elastic contribution may be derived from the statistical theory of rubber elasticity [27]. In this theory it is assumed that the crosslinks are introduced in the solid state. According to Flory [27] the elastic contribution is:

$$(\Delta \mu_1)_{el} = RT v_1 v_e [(\xi_{2,s})^{\frac{1}{3}} - \frac{\xi_{2,s}}{2}]$$
(2.25)

In this equation,  $v_1$  denotes the molar volume of the swelling agent [10,27,45].

The last contribution in equation (2.22) is related to the ionization of the polymer network. For uncharged gels, the magnitude of this ionic contribution is zero, but for charged gels a Donnan-equilibrium problem must be solved [48,49]. This ionic contribution stimulates swelling of the gel and increases with increasing temperature in case of constant volume. In the case of a charged network, there are mobile ions that can go back and forth between the gel and the surrounding medium and there are fixed charges restricted to the gel phase. Assume that a highly swollen polymeric network can be approximated by a dilute polymer solution. In this case, the left-hand side of equation (2.23) can be written in terms of concentrations:

$$(\Delta \mu_1^*)_{ion} - (\Delta \mu_1)_{ion} = v_1 RT \sum_j (c_j - c_j^*)$$
(2.26)

$$(\Delta \mu_1^*)_{ion} = \mu_1^* - \mu_1^0 = RT \ln a_1^*$$
(2.27)

Here,  $c_j$  and  $c_j^*$  denote the concentration of swelling agent within the gel and in the external solution respectively and  $a_1^*$  the activity of the electrolyte.

If the (for example negatively charged) network is swollen in a 1:1 electrolyte and if the concentration of counterions on the polymer is  $i\xi_{2,3}/z_+v_u$  (where  $v_u$  is the molar volume of the structural unit of the polymer), then the ionic contribution can expressed as follows:

$$(\Delta \mu_1^*)_{ion} - (\Delta \mu_1)_{ion} = v_1 RT \ (i \frac{\xi_{2,s}}{z_* v_u}), \qquad if \quad c_s^* \ll \frac{ic_2}{z_*}$$
(2.28)

$$(\Delta \mu_1^*)_{ion} - (\Delta \mu_1)_{ion} = v_1 RT \ [\frac{i^2 (\xi_{2,s})^2}{4I v_{\mu}^2}], \qquad if \quad c_s^* \gg ic_2$$
(2.29)

The symbol i represents the degree of ionization of the polymer,  $z_{i}$  is the charge on the polymer backbone and  $c_{2}$  the polymer concentration. The symbol *I* represents the ionic strength of the electrolyte ( $I=z_{+}z_{.}\nu c_{s}^{*}/2$ ). The first equation (2.28), describes the case in which the external electrolyte concentration  $c_{s}^{*}$  is small compared to the concentration of



Figure 2.16: Schematic presentation of gel structure, a) network structure, b) multiple layers parallel to heat flow and c) multiple layers perpendicular to heat flow [44].



Figure 2.17: Thermal conductivity of polyacrylamide gels according to Hirata's model [44].

counter-ions belonging to the polymer,  $ic_2/z_+$ . In the other case the concentration difference of the mobile electrolyte between the inside and outside of the gel,  $c_s^*-c_s$ , is comparable in magnitude to the concentration of counter-ions. To anionic gels the following relationship between i and the pH of the solution applies:

$$i = \frac{K_a}{10^{-pH} + K_a}$$
(2.30)

where  $K_a$  is the dissociation constant of the carboxylgroup. Substitution of equation (2.30) into equations (2.28) and (2.29) yields:

$$(\Delta \mu_1^*)_{ion} - (\Delta \mu_1)_{ion} = \nu_1 RT \ [\frac{K_a}{10^{-pH} + K_a}](\frac{\xi_{2,s}}{z_*\nu_u})$$
(2.31)

$$(\Delta \mu_1^*)_{ion} - (\Delta \mu_1)_{ion} = \frac{\nu_1 RT}{4I} \left[\frac{K_a}{10^{-pH} + K_a}\right]^2 (\frac{\xi_{2,s}}{\nu_u})^2$$
(2.32)

Combining the mixing, elastic and ionic contributions leads to the swelling equilibria:

$$v_{1} \left[\frac{K_{a}}{10^{-pH} + K_{a}}\right] \left(\frac{\xi_{2,s}}{z_{*}v_{u}}\right) = \ln(1 - \xi_{2,s}) + \xi_{2,s} + \chi_{1}(\xi_{2,s})^{2} + v_{1}v_{e}\left[\left(\xi_{2,s}\right)^{\frac{1}{3}} - \frac{\xi_{2,s}}{2}\right] \qquad if \quad c_{s}^{*} \ll \frac{ic_{2}}{z_{*}}$$

$$(2.33)$$

$$\frac{v_1}{4I} \left[ \frac{K_a}{10^{-pH} + K_a} \right]^2 \left( \frac{\xi_{2,s}}{v_u} \right)^2 = \ln(1 - \xi_{2,s}) + \xi_{2,s} + \chi_1(\xi_{2,s})^2 + \left[ v_1 v_e \left[ \left( \xi_{2,s} \right)^{\frac{1}{3}} - \frac{\xi_{2,s}}{2} \right], \quad if \ c_s^* \ge ic_2$$

$$(2.34)$$

Chandy and Rajasekharan Pillai [15] studied the equilibrium water content of polyacrylamide copolymer hydrogels and the effect of crosslink density and nature of crosslinks on the water sorption and binding behaviour. Among the crosslinkers they studied was N,N'-methylenebisacrylamide, crosslink densities were varied from 5 till 20 mole%. The monomer+crosslinker concentration in the pregel solution was 10%. The equilibrium water content as a function of the mole% crosslinking at 27°C is given in figure 2.19.



Figure 2.18: Weight ratios of unfrozen water  $(m_u)$  to total water  $(m_r)$  and to dry polymer  $(m_p)$  in swollen PVA films. H is the mass fraction of water [34].



Figure 2.19: Equilibrium water content of acrylamidebased gels vs. crosslink density for different crosslinking agents [15].

Rodin *et al.* [13] prepared polyacrylamide gels with a polymer concentration in the range 5 to 15 %P in the pregel solution and crosslink densities varying from 0.06 to 16.7 mole%. They found an empirical formula that could be used to predict the equilibrium swelling at room temperature of their gels.

$$\frac{m_2}{m_1} = 0.483 \left(\frac{c_{NNMBA}}{c_{AAm}}\right)^{-0.335}$$
(2.35)

Here,  $m_2$  denotes the mass of the gel after swelling to equilibrium and  $m_1$  the mass before swelling. In this equation, the concentrations of the acrylamide monomer and N,N'-methylenebisacrylamide crosslinker are expressed in mass %.



Figure 3.1: Measurement setup for determining the thermal properties with the Isomet method.

#### 3 Experimental work

#### 3.1 Synthesis of polyacrylamide gels

The polyacrylamide gels were prepared in aqueous solution by free radical polymerization [9,10,11,12,13]. The chemicals were obtained from Sigma-Aldrich Chemie B.V.:

-Acrylamide, 97%,  $H_2C$  = CHCONH<sub>2</sub>, stabilized with 25-30 ppm cupric ion, catalog no. 14,857-1

-N,N'-Methylenebisacrylamide, 99%, (H<sub>2</sub>C=CHCONH)<sub>2</sub>CH<sub>2</sub>, catalog no. 14,607-2

-N,N,N',N'-Tetramethylethylenediamine, 99%, (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> catalog no. T2,250-0

-Ammonium persulfate, 98%, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, free radical initiator, catalog no. 21,558-9.

The gels were synthesized with different geometries for the various experiments. The microwave heating experiments required cylindrically shaped samples, the inverse photopyroelectric technique and the rheological experiments disc-shaped samples of uniform thickness.

The acrylamide (AAm) monomer and the N,N'-methylenebisacrylamide (NNMBA) crosslinker were dissolved in demineralized water. N,N,N',N'-tetramethylethylenediamine (TEMED) was added as an accelerator and a solution (0.046 M) of ammonium persulfate (AMPS) was used for the initiation of the reaction. Gels with different molar ratios of AAm and NNMBA were prepared. The polymerization took place within one hour at ambient temperature. Tables A.1-A.7, appendix A, give an overview of the gels obtained in this way. After preparation the gels were stored in a refrigerator in sealed dishes and bottles until the measurements were performed.

#### 3.2 Rheological experiments

The polyacrylamide gels were prepared with different amounts of crosslinker added. Rheological experiments were performed to verify whether the synthesis was successful. The rheological experiments required disc shaped samples of uniform thickness. These were obtained by polymerization of the reaction mixture between two glass plates kept at a distance of 2 mm by two glass spacers, see figure 3.5. The experiments were performed for batch 14 polyacrylamide gels at ambient temperature on ARES 4\A18 equipment from Rheometric Scientific. The frequency range was 0.01-100 rad/s.

## 3.3 Water

Since the swelling behaviour of gels is known to depend on the presence of ions in the swelling agent and on the acidity of the swelling agent, the different kinds of water available were tested. The gels studied in this project are assumed to be uncharged and they should

therefore not respond to differences in ion concentration. If they do, however, this could indicate that some hydrolysis has taken place during storage. For these tests normal tap water, demineralized water, distilled water, water both demineralized and distilled and water from a Millipore system were used. The conductivity measurements were performed with a YSI Model 32 Conductance Meter from Yellow Springs Instrument Co. Inc. The acidity was determined with a pH-meter, type Mettler Delta 340.

The swelling of batch 5, 9 and 12 in demineralized water was determined. Small pieces were cut off and weighed. They were put in bottles with demineralized water and kept at room temperature for several days. The water was refreshed regularly. After swelling the surface of the pieces of gel was carefully wiped off with filtering paper and the samples were weighed again. From these results the new polymer concentrations (in %P) were calculated for the gels in swollen state.

Furthermore, swelling experiments of batch 9 in salt solutions were performed to test the dependence of the swelling on the presence of ions. For these experiments sodium thiosulfate pentahydrate [50] <sup>1</sup> (Aldrich 99.5%, A.C.S. reagent,  $Na_2S_2O_3.5H_2O$  catalog no. 21,724-7) was used.

#### 3.4 Thermal properties

When gels are going to be applied as heat storage media, it is important to know their thermal properties, for example the specific heat capacity and the thermal conductivity. These properties can be helpful in gaining insight in the behaviour of the gel upon heating and cooling when it is put into use as a heat or cold storage device. The thermal properties have been determined using two different methods, the first (Isomet) is based on analysis of the temperature response of the gel to heat pulses and the other is inverse photopyroelectric analysis [51]. In the latter method, the thermal properties are determined by using thermal waves and a pyroelectric sensor film. The current response of the film depends on the thermal properties of the sample.

#### 3.4.1 Isomet

The thermal properties, namely the thermal conductivity, the volume thermal capacity and the thermal diffusivity, were determined with an Isomet model 104 instrument from Applied Precision Ltd. supplied with a surface probe. Note that this method determines the volume thermal capacity instead of the specific heat capacity. The volume thermal capacity of a

<sup>&</sup>lt;sup>1</sup> Sodium thiosulfate pentahydrate is a salt with a large heat of crystallization. A former objective of this project was to incorporate this salt in the gel to enhance the heat storage capacity. However, the incorporation of this salt in the gel is complicated and needs to be studied more thoroughly.



Figure 3.2: Measurement setup and sample holder used in the IPPE method for measuring the dynamic thermal properties.



Figure 3.3: Configuration of an inverse photopyroelectric cell. The thermal waves generated by a modulated laser enter the pyroelectric PVDF sensor-film on the left-side [53].

material is the product of its specific heat capacity and its density. These measurements were performed on batch 12 polyacrylamide gels with different crosslink densities, containing 10% polymer. Before the measurements took place, the gel surface was carefully rinsed with water and directly wiped off with filtering paper.

The measurement setup is shown in figure 3.1. The probe is placed directly on the gel surface. The equipment automatically evaluates a temperature baseline before starting the actual measurements. The temperature standard deviation limit for this baseline was 0.02 °C. The heat flow is excited by electrical heating of the probe resistor. The temperature of the probe is monitored by a semiconductor sensor. The thermal properties are calculated according to a built-in mathematical model of heat transfer. The measurements on all samples were performed 11 times in order to reduce the standard deviation of the results. Since the time of measurement is about 20 minutes, the gel with the probe on top of it was covered with parafilm to prevent evaporation of water from the sample surface.

## 3.4.2 Inverse photopyroelectric analysis

The IPPE method is described by Wübbenhorst *et al.* [52]. The measurement setup is given in figure 3.2. In normal photopyroelectric analysis, the heat waves, generated by a modulated laser, enter the sample at the front side. Typical for inverse photopyroelectric analysis is that the heat waves enter on the side of the detector instead of on the sample side. This is shown in close-up in figure 3.3 [53]. The advantage of this method is that the sample thickness is not limited. The detector is a pyroelectric foil, which is metallized on both sides in order to collect the electrical charges generated by the temperature variation. The rear side of this film is blackened with paint to improve the absorption of the incident radiation. Due to the absorption of the radiation, the temperature increases. It can be assumed that all heat is lost to the sample since the thermal properties of the surrounding air are very poor and therefore heat loss to the air will be negligible. Furthermore the pyroelectric film is very thin and consequently there will be no temperature gradient in this film.

When the laser is modulated sinoïdally, the response current can be expressed as a complex quantity. The phase lag of the response signal will increase with the penetration depth of the heat waves. When the pyroelectric current is measured for a series of frequencies a pyroelectric spectrum can be obtained. From this spectrum, the thermal effusivity  $\eta$ , also called heat penetration coefficient, can be calculated. Chirtoc and Mihailescu [54] and Ziel [55] derived a model for the calculation of the thermal effusivity from the (complex) pyroelectric current. It assumes that the situation can be described by one dimensional heat flow into a homogeneous semi-infinite solid. Wübbenhorst [52] derived an approximation for this solution, which allows one to calculate the sample's effusivity directly from the real part

of the pyroelectric current. When the sample is thermally thick compared to the detector, the thermal effusivity can be calculated with the following formula:

$$\eta_s = \sqrt{\pi f} \quad C_d \rho_d L_d \frac{I_d}{Re(I_{ds}^*(f))}$$
(3.5)

Here,  $\eta_s$  is the thermal effusivity of the sample, which is equal to  $\sqrt{\lambda}C_p\rho$ . the symbol f denotes the frequency,  $C_d$  the specific heat capacity of the detector (in this study a poly(vinylidene fluoride) foil),  $\rho_d$  the density of the detector,  $L_d$  the thickness of the detector,  $I_d$  the pyroelectric current obtained for a detector without sample and  $I_{ds}$  the pyroelectric current when a sample is present. The pyroelectric current for a detector without sample can also be obtained from the pyroelectric spectrum. At high frequencies, the penetration depth of the heat waves is very small and the sample does not contribute to the pyroelectric response. The product of specific heat capacity and density  $C_d\rho_d$  of poly(vinylidene fluoride) is 2.3 .10<sup>6</sup> J/m<sup>3</sup>K [52].

The thermal effusivity of batch 13 polyacrylamide gels with different crosslink density was measured by means of inverse photopyroelectric analysis. The measurement frequency was 0.1 Hz- 100 kHz. The experiments were performed at ambient temperature.

A special sample holder was developed for the analysis of gels. This sample holder enables measurement of the gel without the risk of evaporation of water from the surface. A schematic presentation of this sample holder is also given in figure 3.2. It consists of a disc-shaped aluminum holder with an aluminum lid. The pyroelectric sensor film is placed directly on top of the gel. The lid contains a hole ( $\phi = 1$ cm) for the inlet of the modulated laser beam (785 nm). The gel is kept in place by means of rubber rings. During measurement the sample holder was placed in a Petri dish containing water. Through a hole ( $\phi = 1$ cm) in the bottom of the sample holder the water could make contact with the gel, which prevented drying of the gel. A poly(vinylidene fluoride) (PVDF) film with a thickness of 9  $\mu$ m was used as pyroelectric detector. This film is kept in place by an electrically insulated ring. The signal from the sensor was amplified and send to a computer.

#### 3.5 Microwave heating

Since gels consist mainly of water, they are easily and quickly heated in a microwave oven. Some experiments have been performed on batch 10 polyacrylamide gels containing 10 % polymer. The experiments were performed in a microwave oven from Sharp, type Invertor micro-1000W. A chromel-alumel thermocouple was placed inside the oven to register the temperature of the gel. The thermocouple was connected to an x-t-recorder in order to monitor the heating of the polyacrylamide gel, see figure 3.4.


Figure 3.4: Experimental setup used for microwave heating time measurements. As buffer water was used.



Figure 3.5: Mould used for making samples for the rheological tests.

Since the gel samples were very small (mass 20g) an extra load of 300 ml water was used to prevent the radiation from being reflected back to the source which will damage the microwave oven. The positions of the sample and the water load were fixed. Furthermore, because of the limited sample size, the power chosen was 200 W. The samples were shaped cylindrically with a small hole at half height on the axis of the cylinder, to ensure that the thermocouple was always placed at the same position inside all samples.

## 3.6 Differential scanning calorimetry

When gels are to be used as cold storage materials it must be possible to freeze them. Since they consist mainly of water, the freezing behaviour is expected to be similar to that of water. However it is likely that the presence of the polymer will influence, for example, the freezing temperature. To study this effect differential scanning calorimetry has been performed on unswollen batch 9 gels (containing 10% polymer) and swollen batch 9 gels (less then 10% polymer) and on unswollen batch 12 gels (containing 10% polymer). Furthermore, the DSC results can be used to analyze the amount of frozen water in the gels. As is known from literature (see also chapter 2), that water in the gel which shows interaction with the polymer chains, the bound water, will not freeze near 0°C, but at a lower temperature. The thermograms obtained with DSC can be used to study the effect of the crosslink density on the amount of frozen and non-frozen water in the gel.

These experiments were performed on a Perkin-Elmer DSC-7. The samples, weighing about 5 mg, were first cooled from  $20^{\circ}$ C to  $-40^{\circ}$ C at a cooling rate of  $5.0^{\circ}$ C/min. The samples were then kept at  $-40^{\circ}$ C for one minute to ensure that crystallization was complete and were then heated to  $20^{\circ}$ C again at a heating rate of  $5.0^{\circ}$ C/min. The same has also been done on a pure water sample as a reference to be able to calculate the percentage of freezing water in the gels.

## 3.7 Thermogravimetric analysis

The evaporation of water from the polyacrylamide gels has been studied by means of thermogravimetric analysis. The thermogravimetric experiments were performed using a Perkin-Elmer TGA-7 in air. Isothermal experiments at 80°C were performed on polyacrylamide gels, batch 6, with different crosslink ratios and containing 20% polymer. Isothermal experiments at 30°C were performed on batch 14 gels with different crosslink densities and containing 10% polymer. These gels were also used for non-isothermal experiments. The temperature was raised from 25°C till 275°C with a heating rate of 10°C/min. Furthermore, thermogravimetric analysis has been performed on water samples and on a solution of the catalyst N,N,N',N'-tetramethylethylenediamine and the initiator ammonium persulfate in water. The concentration of the initiator and catalyst in this solution were the same as in the gels. Additionally, the reproducibility of the method was tested by isothermal analysis, two of these samples were heated to 80°C and 100°C respectively.

## 4 Results and discussion

## 4.1 Synthesis of polyacrylamide gels

The appearance of the gels is listed in tables A.8 and A.9, appendix A. The gels with crosslinker:monomer ratios 1:5 (about 17 mole% crosslinker) and 1:10 (about 9 mole% crosslinker) showed a white colour. This indicates that the gel structure is heterogeneous and that phase separation has occurred. The gels with ratio 1:25 (about 4 mole% crosslinker) also exhibited some phase separation but were not completely opaque. The other gels with lower crosslink densities were completely transparent. This trend is the same for all the batches. The gels of the different batches were prepared in moulds of different shapes resulting in a different heat flow and temperature profile during polymerization, but this did not lead to large differences in turbidity. These results do not agree with those of Chandy [15] and Gehrke *et al.* [16], see chapter 2. Chandy found that gels with crosslink densities of 5 and 10 mole% were still transparent and that gels with 1.88 mole% crosslinker were opaque when prepared at room temperature. The results of Chandy and Gehrke also do not agree with each other. This can be explained by differences in reaction temperature and initiator concentration in the reaction mixture.

## 4.2 Rheological experiments

In figures B.1 and B.2, appendix B, the results of the rheological experiments are given. The moduli are frequency independent in this range and the loss moduli are lower than the storage moduli which confirms the solid-like behaviour. The theoretical moduli were calculated using equation (2.7), chapter 2, where the functionality of the N,N'-methylenebisacrylamide crosslinker is 4. The molar mass of the crosslinker was 154 g/mole and the density is taken equal to that of pure water, since the 90% of the reaction mixture was water. The temperature during polymerization was taken 300 K. The mass fractions of crosslinker in the systems were calculated from values obtained during synthesis.

The theoretical and experimental values for the equilibrium modulus can be found in figure B.3, appendix B and table H.18, appendix H. The theoretically obtained values are much higher than the experimentally obtained moduli. This is mainly due to the large amount of solvent present during polymerization (about 90% of the reaction mixture was water), which can lead to network imperfections, such as dangling ends and loops. From figure B.1 and table H.18 it can be seen that the modulus increases with increasing crosslink density as expected. The moduli of the 9.12% and 3.85% crosslinker gels are lower than expected. An explanation for this may be found in the fact that these gels showed some phase separation. When these values are compared to literature, see table 2.1, chapter 2, they are all found to be higher. This may be due to the fact that the synthesis procedure was slightly different.

#### 4.3 Water

The results of the conductivity and acidity measurements on water are presented in table H.1, appendix H. The same has been done for the salt solutions used for the swelling experiments, table H.2. It can be seen from table H.1 that the difference in conductivity for distilled, demineralized, millipore and distilled+demineralized water is not very large. However, the conductivity of tap water is much higher. Table H.2 gives the conductivity of the salt solutions used for the swelling experiments. The conductivity of tap water lies in this range.

For the swelling experiments in demineralized water batch 5, 9 and 12 gels were used. The results of these experiments are shown in figures C.1-C.3. In these figures the swelling is given as %P, which is the percentage of polymer in the gel. Thus, the percentage of polymer in this figure decreases with increasing swelling of the gel. The swelling is plotted as a function of the extent of crosslinking in mole%. The swelling of the batch 9 gels was determined every day during four days. The error made during the weighing procedure is  $\pm$  3mg, ( $\leq 0.6\%$ ). In figures C.2 and C.3 also the swelling predicted by Rodin *et al.* [13] is plotted.

Figures C.1-C.3 show that swelling increases when the extent of crosslinking is decreased. This can be explained by the decreasing elasticity of the polymer network. The value of 7.5 . %P for the 9.10 mole% X gel of batch 9 is too low, this can probably be ascribed to damage of the gel during storage. The same gel in batch 12 shows a value of 9.49 %P. From figure C.1 it can be seen that swelling does not increase after more than one day of immersion in water.

Furthermore, in figure C.3 the swelling curve of batch 5 gels is given. Comparing this curve to the one of the batch 12 gels reveals that the gels characterized by about 3.9 mole% X, 2 mole% X and 1 mole% X of this batch show less swelling. For the batch 5 gels the amount of polymer after swelling is 17.2, 14.5 and 10.1 %P respectively. In the case of batch 12 the percentages are 9.07, 8.84 and 7.69 %P. The batch 5 gels were initially prepared with 20%P, the batch 12 gels with 10%P. Thus the concentration of the reaction mixture influences the formation of the network. In chapter 2, figure 2.19, the equilibrium water content of polyacrylamide gels (10% polymer at preparation) is given as determined by Chandy [15]. The water content of these gels is about 80%. This is remarkable since at preparation they contained 10% polymer and 90% water. However, Chandy [15] dried the gels after preparation and before swelling at 80°C.

In figures C.2 and C.3 also the swelling predicted by Rodin *et al.* [13] is plotted. Rodin *et al.* prepared gels containing 5, 10 and 15 %P. It can be seen from these figures that his prediction holds very well for the batch 5 gels prepared with 20 %P but not for the batch 12 gels prepared with 10 %P. No satisfying explanation was found for this discrepancy.

The 1.02 and 16.7 mole% crosslinker gels of batch 9 were also swollen in salt solutions of different molarity. The results are presented in figure C.4. Here the swelling (expressed as a polymer percentage) is plotted versus the salt concentration of the solution. The swelling of the gels turns out to be independent on the salt concentration of the solutions and is comparable to the swelling in demineralized water. This was expected since the gels used have no charges present on the network.

Furthermore swelling experiments in tap water were performed for batch 12 gels with different crosslink densities. The swelling curve is given in figure C.5. The swelling in tap water is only slightly higher than in demineralized water.

## 4.4 Thermal properties

#### 4.4.1 Isomet data

The thermal diffusivity, thermal conductivity and the volume thermal capacity ( $\rho C_p$ ) of the batch 12 polyacrylamide gels as determined with the Isomet method are given in figures D.1 and D.2, appendix D. The thermal properties were measured on gel samples containing 10% polymer. From these figures no relationship can be seen between the thermal conductivity  $\lambda$ , the product of specific heat capacity and density  $\rho C_p$ , thermal diffusivity  $\alpha$  ( $\alpha = \lambda / \rho C_p$ ) and the crosslink density. This may probably be ascribed to poor thermal contact between the sensor and the gel. The temperature during measurement was about 1°C higher for the 1.20% and 2.19% crosslinker gels. This is probably the cause of the small rise in thermal conductivity and the small decrease in specific heat capacity. The thermal conductivity of water is 0.60 W/mK and the specific heat capacity 4.18 kJ/kgK [56]. With a density of 998 kg/m<sup>3</sup> the product  $\rho C_p$  becomes 4.17 .10<sup>6</sup> J/m<sup>3</sup>K. The thermal diffusivity of pure water is thus 0.14  $.10^{-6}$  m<sup>2</sup>/s. According to Hirata [44] the thermal conductivity at room temperature of a polyacrylamide gel containing 10% polymer is 0.55 W/mK and the specific heat capacity 3.95 kJ/kgK. This results in a thermal diffusivity of 0.14 .10<sup>-6</sup> m<sup>2</sup>/s (density of the gel 1.03 .10<sup>3</sup> kg/m<sup>3</sup>). The thermal diffusivities found here are about a factor 10 higher. The thermal effusivities  $(\eta = \sqrt{\lambda}C_{p}\rho)$  were also calculated. The results are given in table H.8. These are of the same order of magnitude as the value for the 10% polymer gel of Hirata  $1.50~.10^3~J/m^2Ks^{\prime\prime}$  and the value for water  $1.58~.10^3~J/m^2Ks^{\prime\prime}.$ 

## 4.4.2 Inverse photopyroelectric analysis

The (dynamic) thermal effusivity of the batch 13 gels with different crosslink densities was determined by the IPPE method. The results are given in figures D.3-D.7. and in table D.1, see appendix D. The thermal effusivities were calculated using equation (3.5). The values for the pyroelectric current of the detector and samples, read from the plots, are also given in table D.1. The product of specific heat capacity and density  $C_d\rho_d$  of PVDF is 2.3 .10<sup>6</sup> J/m<sup>3</sup>K [52], and the thickness of the PVDF sensor film was 9  $\mu$ m. The order of magnitude of the effusivities obtained is in agreement with those of the Isomet method and with the

theoretical values for water and that of the 10% polymer gel of Hirata. However, it was difficult to obtain accurate spectra and therefore the effect of the crosslink density is still unclear.

#### 4.5 Microwave heating

The microwave heating times of polyacrylamide batch 10 gels, 10 %P were determined. The heating time (time until 100°C was reached) is presented as a function of the extent of crosslinking in figure E.1, appendix E, for gels with a mass of 20 g. The heating time for a water sample of the same volume was much larger, namely 4.6 min. During the measurements it turned out that the gel was only locally heated near the position of the thermocouple. Presumably, the thermocouple is also heated in the microwave oven. The temperatures and heating time measured are therefore not reliable. The problem of local heating was not observed when a pure water sample was used. Furthermore the microwave oven was switched on without a sample present. In this case also a temperature raise could be observed, which proves the effect of the thermocouple.

## 4.6 Differential scanning calorimetry

Differential scanning calorimetry was performed on swollen and unswollen (10%P) gels of batch 9 and on unswollen 10 %P gels of batch 12. Figures F.6-F.8, appendix F, show the parts of the heating scans where the glass transitions of the gels occur. The scans obtained on cooling are presented in figures F.9-F.11. The complete heating scans are given in figures F.12-F.14. The thermograms of samples of demineralized water are also given in these figures.

In figures F.1 and F.2 the glass transition is plotted as a function of the extent of crosslinking. The glass transition temperature is found to increase with crosslink density. The 10 %P and swollen batch 9 gels show that the glass transition increases with water content. Normally one would expect it to decrease, due to a plasticizing effect [57]. However, the water content in gels is very high and the glass temperatures are below the freezing-point of water. When the ice-crystals formed in the gel hinder the polymer chain movement, this may explain the observed effect. The glass transition of the 16.7 mole% X gels could not be determined. The glass transitions were partially overlapped by the melting peak of ice which obstructed their determination.

The amount of frozen water in the gels was calculated from both the heating and the cooling scan. The percentage of frozen water is given as a function of the mole percentage crosslinker in figures F.3 and F.4. The curves for the swollen batch 9 gels lie above the 10 %P gels, which was to be expected since these gels contain more water. The expected trend (more frozen water at decreasing crosslink percentages) cannot be observed.

According to Chandy [15], see figure 2.11 in chapter 2, the amount of frozen water is much lower, varying from 40 to 50%. From figure 2.18, the frozen water content can be calculated for gels containing 90% water and 10% polymer (H=0.9). For the unfrozen water ratios  $m_u/m_t=0.2$  and  $m_u/m_p=0.9$  can be read from the plot. From these values a frozen water content of 74% can be calculated. This result agrees with the values obtained in this study, which lie in the range of 70-81%.

Figure F.5 shows the freezing-point of the batch 9 and 12 gels which follows from the DSC thermograms. The freezing-point of pure water in the DSC was -17.0°C. It is not obvious from this figure, how the presence of polymer influences the freezing temperature of the gels. The inaccuracy of the results can be attributed to the fact that the samples were not equally shaped. Additionally, the heterogeneity of the gels with higher crosslink density is also an important factor, since the samples for DSC analysis were very small. When the thermograms, figures F.9-F.14, are compared to those obtained by Higuchi and Iijima [34] it follows that their peaks are wider. However Higuchi and Iijima used a higher heating and cooling rate (10K/min). Unfortunately the area of their peaks is not given in their article. As was already discussed in chapter 2, they found two melting peaks at low water content of the gels in this study is 90%, this may also be the case here. This might explain the shape of the melting peaks in the heating thermograms. Higuchi and Iijima found that freezing occurred at -18°C (255K) for gels containing 71% water.

#### 4.7 Thermogravimetric analysis

The loss of water of the polyacrylamide gels with different crosslink density was determined by thermogravimetric analysis. For the thermogravimetric analysis unswollen batch 6 polyacrylamide gels were used. These gels contained 20% polymer and 80% water. The TGA curves can be found in figure G.1, appendix G. Here the sample weight, expressed in percentage of the weight at start, is given as a function of time. Also the temperature is given as a function of time. No trend in the order of the curves with the crosslink percentage can be observed. This might be due to the fact that the weight of the gels at the start of the experiments could not be determined accurately. This method requires only very small samples which have unfavourable surface/volume ratios. The water in the gels will evaporate relatively fast. This can be seen at the end of the curves. The samples contained 20 mass% polymer, but all curves end at higher percentages.

The isothermal TGA curves at  $30^{\circ}$ C for water and a solution of N,N,N',N'tetramethylethylenediamine and ammonium persulfate in water is shown in figure G.2. The analysis of the initiator and catalyst solution has been performed to examine their influence on the result, especially the final weight of the samples after analysis. The concentration of the solution was the same as those in the gels, so the expected final value of this experiment is 0.21%. From table G.2 it can be seen that the final value of the TGA curve for the solution is 0.2% and that of water 0.0%. Therefore, it is possible that the final values for the gels are also 0.2% higher than expected. The derivative of the curves is also plotted in figure G.2. The derivative is found to be almost constant for water indicating -as expected- a constant evaporation rate and slightly increasing for the initiator and catalyst solution.

In figure G.3 the isothermal TGA curves at  $30^{\circ}$ C are given for 5 samples of a polyacrylamide gel containing 10% polymer and a crosslink density of 0.67%. These experiments have been performed to examine the effect of initial sample size on the curves. The initial weight of these samples is given in table G.2 (0.67% crosslinker gels). From figure G.3 it can be seen that a higher initial sample weight results in a higher curve. The smallest samples evaporate faster. This is probably due to the higher surface/volume ratio and also shorter diffusion lengths inside the sample.

Two of the experiments on the 0.67% crosslinker gels were performed with a two step program. After the first isothermal step at 30°C these gels (sample no. 6 and 8) were heated to 80°C and 100°C, respectively. This has been done to verify whether all the water in the gel would evaporate at the relatively low temperature of 30°C. The results are shown in figures G.4 and G.5. From the latter it can be observed that extra weight loss occurs at the moment the temperature is raised. In table G.2 it can be seen that the final values 11.6% and 11.8.% are in accordance with the other samples of the 0.67% crosslinker gel. The size of the steps at the temperature rise is 0.5% for sample 6 and 0.7% for sample 8. These percentages are very low.

Isothermal analysis of the loss of water at 30°C was also performed on gels with different crosslink densities; the results can be found in figure G.6. It was expected that water in the gels with the lowest crosslink density would evaporate faster than the ones with higher crosslink density. However, no such trend can be seen from this figure. The order of the curves is mainly determined by the initial sample weight. The derivatives of these curves are given in figure G.7. The step observed here is shallower than that of the water curve, figure G.2. It appears that the drying rate is decreased by the presence of the polymer. Nonetheless, the weight of the water samples was smaller than those for the polymer gels, which may also attribute to this effect. The step onsets and heights are given in figure G.8 and table H.17.

Finally, the evaporation rates of these samples have been plotted versus the polymer content of the sample (calculated from the weight loss vs. time curves). The result is given in figure G.9. In this figure two of the three drying periods as determined by Ayer, see figure 2.8, chapter 2, can be seen. The constant drying rate period at the lower polymer concentration side of the plot cannot be observed. For these experiments gels swollen to a higher extent should be used. In table G.1 the amount of unbound water is given for the gels with different crosslink density. These were calculated from the polymer mass% at the intersec-

tion of the two falling-rate lines. According to this method the amount of unbound water is about 10% higher than the amounts determined by differential scanning calorimetry (frozen water%).

Furthermore, TGA experiments have been performed on heating the samples from  $25^{\circ}$ C to  $275^{\circ}$ C with a heating rate of  $10^{\circ}$ C/min. In figures G.10 and G.11 the results of these experiments for 3 water samples are shown. Curve no. 2 is somewhat higher than that of samples no. 1 and 3. This is again due to the difference in initial sample weight, see table G.3). Final values for the sample weight can also be found in this table. These are -0.1%, 0.1% and 0.0% respectively.

These heating experiments were also performed on polyacrylamide gels with different crosslink densities. The results are given in figures G.12 and G.13. Two samples were analyzed of each gel. For this figure one of two samples of each gel was chosen. This has been done in such a way that the initial weights of the curves in the figure show the smallest possible variation. The initial weights vary from 32.4 mg to 37.2 mg. Nonetheless, no relationship can be observed between the crosslink density and the drying rate of the gels. The final weight percentages of the duplicates, see table G.3, agree very well.

Furthermore, it is remarkable that the final weight percentages in table G.3 are lower than those in table G.2. This could indicate that after the low temperature experiments  $(30^{\circ}C)$  the samples are not completely dry. On the other hand, the samples of the higher temperature experiments showed clear signs of degradation afterwards. The polymer had turned yellow and showed blisters. The mass of the samples may well have decreased as a result of the degradation.

## **5** Conclusions

#### 5.1 Synthesis of polyacrylamide gels

From the appearance of the gels it can be concluded that the turbidity increases with crosslink density. The gels with a crosslink density of 3.85% or more showed visible phase separation and were clouded. There was no relation between the turbidity of the gels and the geometry or size of the sample.

#### 5.2 Rheological experiments

When the crosslink density is increased, the equilibrium shear modulus increases. The network formed is far from ideal, as can be seen from the large differences between experimental and theoretical values. The gels which showed phase separation had lower moduli.

## 5.3 Water

The swelling of the gels in water increases when the extent of crosslinking is decreased. The concentration of the components in the reaction mixture influences the swelling of the gels. When the concentration of monomer and crosslinker in the reaction mixture is higher, the swelling of the gels formed will be lower. The gels in which phase separation had occurred also showed less swelling in water.

From the swelling experiments in salt solutions it can be concluded that the swelling of uncharged polyacrylamide gels is does not depend on the salt concentration and that it is comparable to the swelling in demineralized water. The swelling in tap water is only slightly higher than that in demineralized water.

#### 5.4 Thermal properties

The values for the thermal effusivity of the polyacrylamide gels found with the IPPE method were of the same order of magnitude as those obtained with the Isomet method and that of water.

#### 5.5 Differential scanning calorimetry

The glass transition temperatures of all gels were below the melting-point of the gel. The glass transition temperatures of the swollen gels were found to be higher than those of the unswollen gels. The glass transition temperature was found to increase with crosslink density. A relationship between the amount of frozen water and crosslink density could not be observed. The amount of frozen water is higher for the swollen gels.

## 5.6 Thermogravimetric analysis

From the derivatives of the TGA curves, it can be seen that the presence of polymer decreases the drying rate, compared to that of pure water. The relation between the crosslink density and the drying rate is still unclear due to the effect of the variation in initial sample weight. The final sample weights agreed with the theoretically calculated values.

## 6 Suggestions for further research

## 6.1 Synthesis of polyacrylamide gels

It was found that gels with a crosslink density of 3.85% or more showed phase separation. The heterogeneity of the structure of those gels has a profound effect on its properties. To obtain better insight in the influence of the crosslink density on the properties of the gel, more transparent gels should be studied. The best range for the crosslink density would be between 0.2 mole% and 3.85 mole%. In this way transparent, homogeneous gels will be obtained. Furthermore, the structure (heterogeneous/homogeneous) of the gel could be studied by scanning electron microscopy of freeze-dried samples. Also a quantitative measure for the turbidity must be found, for instance spectrophotometry [18]. Furthermore, the gels formed. By adjustment of the initiator and catalyst concentration the temperature and thus the turbidity can be controlled [16].

For the application as heat storage material it will be necessary to study the long-term behaviour at elevated temperatures. It is known from the literature that hydrolysis will increase with temperature [21]. When gels are hydrolyzed to a higher extent, they will be able to absorb more water, which is an advantage. Additionally dielectric spectroscopy can be performed to follow the polymerization reaction.

## 6.2 Rheological experiments

The rheological experiments should be performed for more different crosslink densities in the range 0.2 mole%-3.85 mole% to obtain a better insight the relationship between the modulus and the crosslink density. Furthermore, it might be interesting to perform these experiments on gels containing different amounts of water. Finally it may be necessary to measure the modulus of the gels after freezing and thawing to examine whether the network is damaged on freezing or not.

#### 6.3 Thermal properties

The Isomet equipment of Applied Precision Ltd. is not suitable for the study of the relationship between the thermal properties of the polyacrylamide gels and the crosslink density. The Isomet equipment was originally designed for determining the thermal properties of solid materials.

With inverse photopyroelectric analysis the thermal effusivity of the gels was determined. The measurement setup should be changed in such a way that thinner gel samples can be examined so that the thermal conductivity and specific heat capacity can be determined separately. The values thus obtained can then be used to test the model given by Hirata *et al.* [44], see chapter 2. Moreover, it may also be possible to monitor the water uptake or drying of the gel by the IPPE method, since the thermal properties depend heavily on the water content of the gel.

## 6.4 Microwave heating

The measurement setup for the microwave heat experiments can probably be improved by replacing the thermocouple by some external device to measure the temperature, for instance an infrared camera.

## 6.5 Differential scanning calorimetry

The results of the DSC measurements can be improved by taking equally shaped samples, but this will be difficult to accomplish. Furthermore, it would be interesting to perform the analysis on samples with different water content. Higuchi [34] found that two peaks (due to water in different states) became separated at lower water contents.

## 6.6 Thermogravimetric analysis

It was found that the accuracy of the TGA measurements mainly depends on the initial sample weight. The samples used for the TGA measurements should be equally shaped and should have equal masses. This is difficult to achieve in practice. Another way to minimize the effect of the initial sample weight may be by performing experiments with a large number of samples of the same gel and calculate the average.

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## Appendix A: Synthesis of polyacrylamide gels

Table A.1: Synthesis of batch 5 PAAm gels with different molar ratios NNMBA:AAm, disc shape ( $\phi = 9$ cm, d = 4mm). For initiation 38,2  $\mu$ l TEMED and 11 ml AMPS solution (0.046 M) were added. The total gel volume was 25 ml.

NNMBA : AAm	Mole% X	Mass% P
1:25	3.87	20.0
1:50	2.05	20.0
1:100	1.03	19.9
1:200	0.44	20.0
1:500	0.25	20.0
1:1000	0.10	20.0

Table A.2: Synthesis of batch 6 PAAm gels with different molar ratios NNMBA:AAm, disc shape ( $\phi = 9$ cm, d = 4mm). For initiation 38.2  $\mu$ l TEMED and 11 ml AMPS solution (0.045 M) were added. The total gel volume was 25 ml.

NNMBA : AAm	Mole% X	Mass% P
1:5	16.8	19.9
1:10	9.21	19.0
1:25	3.86	20.5
1:50	1.94	19.9
1:100	1.08	19.9

Table A.3: Synthesis of batch 9 PAAm gels with different molar ratios of NNMBA:AAm. For initiation 76.4  $\mu$ l TEMED and 22 ml AMPS solution (0.046 M) were added. The total gel volume 100 ml.

NNMBA : AAm	Mole% X	Mass %P
1:5	16.7	9.84
1:10	9.10	10.0
1:25	3.87	10.0
1:50	1.96	10.0
1:100	1.02	10.0

Table A.4:Synthesis of batch 10 PAAm gels with different molar ratios NNMBA:AAm, cylinder ( $\phi = 28$ mm,h=32mm).For initiation 15.25 µl TEMED and 4.4 ml AMPS solution (0.046 M) were added. The total gel volume was 20 ml.

NNMBA : AAm	Mole% X	Mass% P
1:5	16.5	9.92
1:10	9.09	9.96
1:25	3.79	10.0
1:50	2.11	10.0
1:100	1.15	10.0

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Table A.5:Synthesis of batch 12 PAAm gels with different molar ratios NNMBA:AAm, disc shape ( $\phi = 9$ cm, d = 4 mm).For initiation 19.1  $\mu$ l TEMED and 5.5 ml AMPS solution (0.045 M) were added. The total gel volume was 25 ml.

NNMBA : AAm	Mole% X	Mass% P
1:5	16.7	9.98
1:10	9.11	10.0
1:25	3.88	10.0
1:50	2.19	10.0
1:100	1.20	10.0

Table A.6: Synthesis of batch 13 PAAm gels with different molar ratios NNMBA:AAm, disc shape ( $\phi = 9$ cm, d=4mm).For initiation 19.1  $\mu$ l TEMED and 5.5 ml AMPS solution (0.046 M) were added. The total gel volume was 25 ml.

NNMBA : AAm	Mole% X	Mass% P
1:10	9.14	10.0
1:25	3.85	10.0
1:50	1.97	10.0
1:100	1.02	9.99
1:150	0.74	10.0
1:200	0.51	10.0

Table A.7: Synthesis of batch 14 PAAm gels with different molar ratios NNMBA:AAm. For initiation 76.4  $\mu$ l TEMED and 22 ml AMPS solution (0.046 M) were added. The total gel volume was 100 ml.

NNMBA : AAm	Mole% X	Mass% P
1:10	9.12	10.0
1:25	3.85	10.0
1:50	1.98	10.0
1:100	1.00	10.0
1:150	0.67	10.0
1:200	0.51	10.0

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NNMBA: AAm	Batch 5	Batch 6	Batch 9	Batch 10
1:5	-	white	white	white
1:10	-	white	white	white
1:25	turbid	turbid	turbid	turbid
1:50	transp.	transp.	transp.	turbid
1:100	transp.	transp.	transp.	transp.
1:200	transp.	-	-	-
1:500	transp.	-	-	-
1:1000	transp.	-	-	-

**Table A.8:** Appearance of polyacrylamide gels of batches 5, 6, 9 and 10. The batches 5 and 6 contained 20% polymer and the batches 9 and 10 contained 10% polymer.

Table A.9: Appearance of polyacrylamide gels of batches 12, 13 and 14. The gels contained 10% polymer.

NNMBA: AAm	Batch 12	Batch 13	Batch 14
1:5	white	-	-
1:10	white	white	white
1:25	turbid	turbid	turbid
1:50	transp.	transp.	transp.
1:100	transp.	transp.	transp.
1:150	-	transp.	transp.
1:200	-	transp.	transp.
1:500	-	-	-
1:1000	-	-	-

## Appendix B: Rheological experiments



Figure B.1: Storage modulus as a function of the frequency for polyacrylamide gels, batch 14, with different crosslink ratios, containing 10% polymer. Experiments were performed in a rheometer at ambient temperature.

PAAm, batch 14, 10 % polymer



Figure B.2: Loss modulus as a function of the frequency for polyacrylamide gels, batch 14, with different crosslink ratios, containing 10% polymer. The experiments were performed in a rheometer at ambient temperature.



Figure B.3: Theoretical and experimental storage moduli of batch 14 polyacrylamide gels.

# Appendix C: Swelling behaviour of polyacrylamide gels



Figure C.1: Swelling of batch 9 polyacrylamide gels in demineralized water vs. mole% crosslinker. The mass %P of polymer in the gel is plotted on the y-axis.



Figure C.2: Swelling of batch 12 PAAm gels in demineralized water vs. mole % crosslinker and swelling curve according to Rodin *et al.* [13]. Note that %P denotes the mass% of polymer.



Figure C.3: Swelling of batch 5 polyacrylamide gels in demineralized water vs. mole% crosslinker and swelling curve according to Rodin *et al.*[13]. %P denotes the mass% of polymer.



Figure C.4: Swelling of batch 9 polyacrylamide gels in solutions of  $Na_2S_2O_3.5H_2O$ . Note that %P denotes the mass percentage of polymer in the gel.

## Swelling of batch 12 in tap water



Figure C.5: Swelling of batch 12 polyacrylamide gels in tap water. The mass %P denotes the polymer content in the gel.

# Appendix D: Thermal properties of polyacrylamide gels



Figure D.1: Thermal diffusivity of batch 12 polyacrylamide gels obtained using Isomet equipment.

Thermal conductivity of PAAm, batch 12, 10%P



Figure D.2: Thermal conductivity and volume thermal capacity ( $\rho C_p$ ) of batch 12 polyacrylamide gels obtained using Isomet equipment.



Figure D.3: IPPE spectrum of polyacrylamide gel, containing 3.85 mole% crosslinker and 10% polymer. Pyroelectric current ( $\bigcirc$  real and  $\bullet$  imaginary part) divided by the root of frequency at ambient temperature.



Figure D.4: IPPE spectrum of polyacrylamide gel, containing 1.97 mole% crosslinker and 10% polymer. Pyroelectric current ( $\bigcirc$  real and  $\bullet$  imaginary part) divided by the root of frequency at ambient temperature.



Figure D.5: IPPE spectrum of polyacrylamide gel, containing 1.02 mole% crosslinker and 10% polymer. Pyroelectric current ( $\bigcirc$  real and  $\bullet$  imaginary part) divided by the root of frequency at ambient temperature.



Figure D.6: IPPE spectrum of polyacrylamide gel, containing 0.74 mole% crosslinker and 10% polymer. Pyroelectric current ( $\bigcirc$  real and  $\bigcirc$  imaginary part) divided by the root of frequency at ambient temperature.



Figure D.7: IPPE spectrum of polyacrylamide gel, containing 0.51 mole% crosslinker and 10% polymer. Pyroelectric current ( $\bigcirc$  real and  $\bullet$  imaginary part) divided by the root of frequency at ambient temperature.

NNMBA: AAm	Mole% X	f (Hz)	L√f (A√s)	f (Hz)	$ \begin{array}{c} \operatorname{Re}(I_{ds}) / \sqrt{f} \\ (A \sqrt{s}) \end{array} $	η (kJ/m²Ks <sup>½</sup> )
1:25	3.85	2.0e03	70	20	1.1e02	1.0
1:50	1.97	6.0e02	2.5e02	6	2.0e02	1.1
1:100	1.02	5.0e02	2.0e02	20	70	2.3
1:150	0.74	5.0e02	1.2e02	30	1.0e02	1.0
1:200	0.51	5.0e02	2.5e02	9	1.1e02	1.9

Table D.1: Thermal effusivity of batch 13 polyacrylamide gels determined by inverse photopyroelectric analysis at room temperature.

# Appendix E: Microwave heating of polyacrylamide gels



Figure E.1: Microwave heating time of batch 10 polyacrylamide gels, 10%P, vs. mole% crosslinker.

## Appendix F: Differential scanning calorimetry



Figure F.1: Glass transition temperature and jump in specific heat capacity of batch 9 polyacrylamide gels vs. mole% crosslinker.



Figure F.2: Glass transition temperature and jump in specific heat capacity of batch 12 polyacrylamide gels vs. mole% crosslinker.



Figure F.3: Frozen water in batch 9 polyacrylamide gels vs. mole% crosslinker.



Figure F.4: Frozen water in batch 12 polyacrylamide gels vs. mole% crosslinker.



Figure F.5: Temperature at which freezing occurs for unswollen (10%P) and swollen batch 9 polyacrylamide gels and unswollen (10%P) batch 12 gels.



Figure F.6: Close-up of DSC heating curves. Glass transitions of batch 9 polyacrylamide gels swollen to equilibrium at room temperature, heating rate 5.0°C/min.



Figure F.7: Close-up of DSC heating curves. Glass transitions of batch 9 polyacrylamide gels 10%P, heating rate 5.0°C/min.



Figure F.8: Close-up of DSC heating curves. Glass transitions of batch 12 polyacrylamide gels, 10%P, heating rate 5.0°C/min.


Figure F.9: DSC thermograms of batch 9 polyacrylamide gels (swollen to equilibrium at room temperature) obtained during cooling at rate 5.0°C/min.



Figure F.10: DSC thermograms of batch 9 polyacrylamide gels (10%P) obtained during cooling at rate 5.0°C/min.







Figure F.12: DSC thermograms of batch 9 polyacrylamide gels (swollen to equilibrium at room temperature) obtained during heating at rate 5.0°C/min.



Figure F.13: DSC thermograms of batch 9 polyacrylamide gels (10%P) obtained during heating at rate 5.0°C/min.



Figure F.14: DSC thermograms of batch 12 polyacrylamide gels (10%P) obtained during heating at rate 5.0°C/min.

## Appendix G: Thermogravimetric analysis



Figure G.1: TGA curves for batch 6 polyacrylamide gels. The temperature is plotted on the right y-axis.



Figure G.2: TGA curves for water and a solution of TEMED and AMPS in water. Isothermal curves at 30°C. The derivatives are plotted on the right y axis.



Figure G.3: TGA curves for 5 samples of polyacrylamide gels, batch 14, containing 0.67 mole% crosslinker and 10% polymer. Isothermal curves showing the loss of water at 30°C.



Figure G.4: TGA curves for PAAM gels, batch 14, 0.67 mole% crosslinker and 10% polymer. 1<sup>st</sup> step isothermal at 30°C, 120 min., 2<sup>nd</sup> step at 80°C for sample 6 and 100°C for sample 8.



Figure G.5: Part of TGA curves (#1 and #3) during a temperature rise for polyacrylamide gels, containing 0.67 mole% crosslinker and 10% polymer.



Figure G.6: TGA curves for polyacrylamide gels with different crosslink ratios, batch 14, containing 10% polymer. Isothermal curves obtained at 30°C.



Figure G.7: Derivatives of TGA curves of polyacrylamide gels with different crosslink ratios, batch 14, containing 10% polymer.



Figure G.8: Step in first derivatives of isothermal TGA curves of batch 14 polyacrylamide gels with different crosslink density.





Figure G.9: Evaporation rate of polyacrylamide gels with different crosslink densities vs. the polymer content in mass%.

Table G.1: Amount of unbound water calculated from TGA experiments for polyacrylamide gels with different crosslink densities, according to Ayer's method [43].

Mole %X	% Unbound water
3.85	86
1.98	86
1.00	84
0.67	88
0.51	86



Figure G.10: TGA curves for water. Heating from room temperature to 275°C at a rate of 10°C/min., the temperature during the measurement is also given (#4).



Figure G.11: Derivatives of TGA curves of water.



Figure G.12: TGA curves of polyacrylamide gels with different crosslink ratios, batch 14, containing 10% polymer, obtained on heating from 25 to 275°C, rate 10°C/min.



Figure G.13: Derivatives of TGA curves of polyacrylamide gels with different crosslinking ratios.

Sample	Mass (mg) at $t=0$	Mass% after meas.
Water	13.9	0.0
TEMED+AMPS in water	13.9	0.2
PAAm gel, 3.85%X (1:25)	17.1	12.6
PAAm gel, 1.98%X (1:50)	18.7	12.5
PAAm gel, 1.00%X (1:100)	23.5	12.0
PAAm gel, 0.67%X, (1:150) no.2	19.9	11.7
PAAm gel, 0.67%X, no.4	36.1	12.3
PAAm gel, 0.67%X, no.5	25.6	11.9
PAAm gel, 0.67%X, no.6	36.4	11.6
PAAm gel, 0.67%X, no.8	31.0	11.8
PAAm gel, 0.51%X (1:200)	13.7	12.1

Table G.2: Sample weight before and after thermogravimetric analysis, isothermal experiments at 30°C. The polyacrylamide gels had different crosslinking ratios and contained 10% polymer.

Table G.3: Sample weight before and after thermogravimetric analysis, heating experiments from  $25^{\circ}$ C to  $275^{\circ}$ C (rate  $10^{\circ}$ C/min.). The polyacrylamide gels had different crosslinking ratios and contained 10% polymer.

Sample	Mass (mg) at $t=0$	Mass% after meas.
Water, no.1	19.8	-0.1
Water, no.2	24.1	0.1
Water, no.3	20.3	0.0
PAAm, 3.85%X, (1:25) no.1	26.3	10.7
PAAm, 3.85%X, no.2	34.5	10.7
PAAm, 1.98%X, (1:50) no.1	31.2	10.2
PAAm, 1.98%X, no.2	32.8	10.6
PAAm, 1.00%X, (1:100) no.1	32.4	10.7
PAAm, 1.00%X, no.2	25.7	10.6
PAAm, 0.67%X, (1:150) no.9	36.7	10.5
PAAm, 0.67%X, no.10	39.5	10.5
PAAm, 0.51%X, (1:150) no.1	25.7	10.7
PAAm, 0.51%X, no.2	37.2	10.7

## Appendix H: Tables

	Conductivity (µS)	pН
Distilled water	1.55	5.43
Demineralized water	1.10	5.60
Millipore	1.91	5.36
Demineralized+distilled water	1.06	5.23
Tap water	500	6.68

Table H.1: Conductivity and acidity of water at 23°C

Table H.2: Conductivity and acidity of  $Na_2S_2O_3.5H_2O$  solutions

Concentration (M)	Conductivity (mS)	pH
8.7e-05	23.6e-03	-
1.8e-04	45.3e-03	-
0.034	6.22	6.64
0.084	11.8	6.39
0.16	23.7	6.36
0.81	84.5	6.39
1.61	120	6.71

NNMBA: AAm	Mole% X	%P 1 day	%P 2 days	%P 3 days	%P 4 days
1:5	16.7	9.32	9.34	9.32	9.29
1:10	9.10	7.51	7.52	7.47	7.54
1:25	3.87	8.77	8.72	8.70	8.71
1:50	1.96	8.37	8.37	8.29	8.35
1:100	1.02	7.15	6.81	6.79	6.79

 Table H.3: Swelling of batch 9 polyacrylamide gels in demineralized water.

Table H.4: Swelling of batch 12 polyacrylamide gels in demineralized water and swelling according to Rodin *et al.* [13].

NNMBA : AAm	Mole% X	%P exp.	%P pred.
1:5	16.7	9.95	15.6
1:10	9.11	9.49	12.4
1:25	3.88	9.07	9.2
1:50	2.19	8.84	7.5
1:100	1.20	7.69	6.1

NNMBA : AAm	Mole% X	%P exp.	%P pred.
1:25	3.87	17.2	18.3
1:50	2.05	14.5	14.7
1:100	1.03	10.1	11.0
1:200	0.44	8.18	8.7
1:500	0.25	7.18	7.3
1:1000	0.10	5.13	5.2

Table H.5: Swelling of batch 5 polyacrylamide gels in demineralized water and swelling according to Rodin *et al.* [13].

Table H.6: Swelling of batch 9 gels in salt solutions expressed in mass percentage of polymer in the gel (%P).

Conc (M)	16.7 %X 1 day	16.7 %X 2 d.	16.7 %X 3 d.	1.02 %X 1 day	1.02 %X 2 d.	1.02 %X 3 d.
8.7e-05	9.37	9.35	9.42	7.03	6.99	6.98
1.78e-04	9.33	9.37	9.37	6.78	6.77	6.75
0.035	9.45	9.49	9.18	6.60	6.42	6.49
0.081	9.20	9.26	9.35	6.41	6.21	6.22
0.16	9.10	9.10	9.30	6.16	5.92	5.97
0.807	8.49	8.64	8.64	5.91	5.22	5.17
1.61	8.15	8.30	8.15	6.44	5.57	5.47

NNMBA : AAm	Mole% X	%P, 1 day	%P,2 days
1:5	16.7	10.2	10.1
1:10	9.11	9.90	9.87
1:25	3.88	9.93	10.0
1:50	2.19	9.86	9.83
1:100	1.20	7.82	7.88

Table H.7: Swelling of batch 12 gels with different molar ratios NNMBA:AAm in tap water.

Table H.8: Thermal properties of batch 12 gels obtained by using Isomet equipment.

NNMBA: AAm	Mole %X	λ(W/mK)	ρC <sub>p</sub> (10 <sup>6</sup> J/m <sup>3</sup> K)	$\alpha(10^{-6}\text{m}^2/\text{s})$	η (J/m²Ks <sup>½</sup> )	Temp (°C)
1:5	16.7	1.33	1.36	0.98	1.34e03	30.7
1:10	9.11	1.33	1.39	0.97	1.36e03	31.0
1:25	3.88	1.33	1.27	1.06	1.30e03	31.2
1:50	2.19	1.46	1.29	1.18	1.37e03	32.0
1:100	1.20	1.70	0.88	2.50	1.23e03	32.0

Table H.9: Microwave heating times of batch 10 polyacrylamide gels. Sample mass was 20 g.

NNMBA : AAm	Mole% X	Time (min)
1:5	16.5	1.10
1:10	9.09	0.90
1:25	3.79	0.70
1:50	2.11	0.65
1:100	1.15	0.60

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NNMBA : AAm	Mole% X	%P	T <sub>g</sub> (°C)	$\Delta C_{p}$ (J/g°C)
1:5	16.7	9.84	-	-
1:10	9.10	10.0	-11.3	1.01
1:25	3.87	10.0	-12.1	1.06
1:50	1.96	10.0	-12.5	1.37
1:100	1.02	10.0	-12.9	1.47

Table H.10: Glass transition temperatures and jump in specific heat capacity of batch 9 gels containing 10%P.

Table H.11: Glass transition temperature and jump in specific heat capacity of swollen batch 9 gels.

NNMBA : AAm	Mole% X	%P	T <sub>g</sub> (°C)	ΔC <sub>p</sub> (J/g°C)
1:5	16.7	9.29	-	-
1:10	9.11	7.54	-8.6	1.14
1:25	3.87	8.71	-10.2	1.67
1:50	1.96	8.35	-10.3	1.72
1:100	1.02	6.79	-10.8	1.34

Table H.12: Glass transition temperature and jump in specific heat capacity of batch 12 gels containing 10%P.

NNMBA : AAm	Mole% X	%P	T <sub>g</sub> (°C)	ΔC <sub>p</sub> (J/g°C)
1:5	16.7	9.98	-	-
1:10	9.11	10.0	-11.5	0.68
1:25	3.88	10.0	-12.3	1.19
1:50	2.19	10.0	-13.6	0.63
1:100	1.20	10.0	-14.8	0.57

NNMBA : AAm	Mole% X	%P	Freezing temp. °C	Frozen water% heat.	Frozen water% cool.
1:5	16.7	9.84	-22.2	73.8	69.2
1:10	9.10	10.0	-15.7	72.3	74.0
1:25	3.87	10.0	-20.1	71.0	70.2
1:50	1.96	10.0	-20.2	73.9	74.3
1:100	1.02	10.0	-19.8	71.4	73.0

Table H.13: Freezing-point and mass% frozen water obtained on heating and cooling for batch 9 gels containing 10%P.

Table H.14: Freezing-point and mass% frozen water obtained on heating and cooling for swollen batch 9 gels.

NNMBA : AAm	Mole% X	%P	Freezing point (°C)	Frozen water% heat.	Frozen water% cool.
1:5	16.7	9.29	-17.6	74.7	73.9
1:10	9.11	7.54	-11.4	80.6	80.8
1:25	3.87	8.71	-20.2	76.3	72.0
1:50	1.96	8.35	-14.5	79.4	81.1
1:100	1.02	6.79	-19.1	81.2	79.0

Table H.15: Freezing-point and mass% frozen water obtained on heating and cooling for batch 12 gels containing 10%P.

NNMBA : AAm	Mole% X	%P	Freezing point (°C)	Frozen water % heat.	Frozen water% cool.
1:5	16.7	9.98	-22.1	74.6	67.0
1:10	9.11	10.0	-18.0	72.3	73.9
1:25	3.88	10.0	-11.1	77.0	81.4
1:50	2.19	10.0	-21.7	74.5	71.7
1:100	1.20	10.0	-22.9	77.4	70.1

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NNMBA: AAm	B.9, swollen, cooling	B.9, swol- len, heating	B.9,10%P, cooling	B.9, 10%P, heating	B.12,10%P, cooling	B.12,10%P, heating
1:5	-252	254	-236	251	-228	254
1:10	-275	274	-252	246	-252	246
1:25	-245	259	-239	242	-277	262
1:50	-276	270	-253	251	-244	253
1:100	-269	276	-248	243	-239	263

Table H.16: Heats of transition in J/g obtained by DSC. Experimentally obtained values for pure water were -302 J/g on cooling and 340 J/g on heating.

Table H.17: Step observed in  $1^{st}$  derivative of TGA curves obtained isothermally at 30°C for polyacrylamide gels with different crosslinking ratios.

Sample	X <sub>midpoint</sub> (min.)	ΔY (%/min.)	X <sub>onset</sub> (min.)	X <sub>end</sub> (min.)
Water	39.1	2.48	34.5	43.6
3.85 %X (1:25)	54.6	0.86	47.3	59.7
1.98 %X (1:50)	56.5	0.95	47.8	63.0
1.00 %X (1:100)	64.3	0.76	56.4	70.9
0.67 %X (1:150)	65.7	1.02	52.3	76.9
0.51 %X (1:200)	39.3	1.82	33.3	44.6

Sample	G' <sub>exp.</sub> (kPa)	G' <sub>theor.</sub> (kPa)	G'exp./G'theor.
1:10 (9.12%)	8.3	580	0.01
1:25 (3.85%)	19.1	259	0.07
1:50 (1.98%)	20.0	136	0.15
1:100 (1.00%)	14.5	69.6	0.21
1:150 (0.67%)	9.6	46.6	0.21
1:200 (0.51%)	8.3	35.4	0.23

Table H.18: Comparison between experimental and theoretical values for the storage modulus of polyacrylamide gels with different crosslink ratios.

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