Macromolecular Chemistry and Physics

Full Paper: Glycidyl methacrylate was reacted in 2methyl pyrrolidone solution with N-methyl-D-glucamine (NMG) to produce N-D-glucidol, N-methyl-2-hydroxy propyl methacrylate (GMHP). The reaction proceeded exclusively via ring opening of the oxirane. The resulting vinyl monomer was a waxy product and soluble in water, ethanol, methanol, DMF, and NMP. Copolymerization of GMHP with N,N'-tetraallyl piperazinium dichloride by the inverse suspension method (water in oil), using a toluene/chloroform (3:1) mixture as continuous phase, led to crosslinked hydrogels in imperfect bead form. Crosslinking was also achieved without using additional crosslinker. Heating of N-methyl-D-glucamine with 10% excess of glycidyl methacrylate in NMP at 60°C for 4 h, resulting the formation of N-methyl-D-glucamine carrying two methacrylate groups. These dimethacrylate groups serve as a crosslinking agents. In situ redox polymerization of the mixture in water led to transparent hydrogels. These hydrogels in the swollen state have been demonstrated to be very efficient sorbents for the removal of boron on ppm levels. The boron loaded polymers can be regenerated by simple acid (0.1 M HCl) and base (0.1 M NaOH) treatment.



Crosslinked polymer gels for boron extraction derived from *N*-glucidol-*N*-methyl-2-hydroxypropyl methacrylate

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Introduction

Water contamination by boron is a widespread enviromental problem, since even a few ppm present in irrigation water can cause stunting of plant growth. Until now, the removal of boron from water is still a challenging problem¹⁾. Since the worldwide largest boron sources are located in Turkey and USA, boron pollution is a severe problem for these countries. For instance, a big area around Menderes river in West Anatolia, suffer from the boron pollution caused by geothermal sources and boron mines. Although a boron-spesific absorption resin emerged in the mid-1960's the removal of boron from waters still remains a problem, since only low amounts of boron could be removed using this resin.

As presented by Deul and Neukom², it is well known, that compounds containing vicinal diol groups are the most efficient materials for the chelation of boron². Various methods for the chelation of boron using furanosides and

piranosides were studied by means of ¹¹B NMR spectroscopy³⁾. These studies showed that diol/boron complexes with a diol/boron ratio of 1:1 or 2:1 are very stable, since five-membered chelates based on vicinal diol groups are easier formed than six-membered rings. Generally, monoborate complexes are largely predominant and the average stability constants of these complexes are about 10. As expected, the chelation is favoured at a higher pH. In acidic media, below pH = 3, the equilibrium of chelation shifts to the adduct side and almost no binding occurs between boric acid groups and diol groups occurs. Therefore crosslinked polymers carrying monosaccaride derivatives were considered for boron sorption and patented⁴⁾. As reported by Bowman and coworkers in 1995, an ultrafiltration membrane containing N-methyl glucamine, grafted onto linear polyepichlorohydrin, is a efficient approach for the removal of boron from water⁵⁾. The only drawback of the method is polymer linkage from the membrane in time.

Recently, we described a crosslinked poly(styrene sulfonamide) carrying sorbitol functions for the chelation of boric acid in ppm levels. However, the capacity was relatively low due to the low degree of sorbitol functionalization⁶⁾. Based on these results, one can deduce, that all the polymers carrying sugar derivatives may be used for boron sorption. In fact, this is true in the presence of buffered solutions. However, in real applications, especially when traces of boron has to be removed, the use of buffer solutions is not practicable. This fact is frequently omitted. The complexation of boron using sugar derivatives like D-glucose, D-sorbitol and D-mannitol accompanies the formation of protons that lowers the ph. Hence, the proton itself, liberated during the complexation, limitates the complexation of boron. In order to overcome this drawback, sugars comprising amine functions, such as Nmethyl-D-glucamine, were used by Yoshimura and coworks for the complexation of boron⁷⁾. Here the overall formation constant of the boron complex is in the range of 10⁴. Obviously, the role of the amine groups is to capture the proton released. The commercial resin (IRA-743) containing N-methyl-D-glucamine groups were proved to be a powerfull sorbent for removal boron traces. It was possible, to reduce the boron concentration upto 1 ppm⁸⁾. However, each regeneration by acid treatment, reduced its capacity about 14%⁹. This can presumably be explained by an acid catalyzed side reaction based on heterocondensation by phenyl rings.

In order to overcome this drawback, in this study we have prepared glycidyl methacrylate based crosslinked polymers containing *N*-methyl-D-glucamine functions. The aliphatic support is expected to prevent the side reaction during the acidic regeneration procedure.

Here, the ester linkage in the glycidyl methacrylate (GMA) based polymers can be considered as a type of bond sensitive towards hydrolysis. Fortunately, this bond shows a reasonable stability against acid and base hydrolyses. Due to this fact, GMA monomer was considered as an alternative key monomer for the synthesis of functional polymers¹⁰.

In the present study, two crosslinked polymers were prepared starting from GMA and *N*-methyl-D-glucamine (NMG). Boron sorption characteristics and regeneration conditions of the crosslinked polymers were investigated.

Experimental part

Glycidyl methacrylate (Fluka), *N*-methyl-D-glucamine (Aldrich), and piperazine (Fluka) were obtained in an analytical grade and used as supplied. NMR spectra were recorded using a Bruker model 200 spectrometer. FT-IR spectra were obtained Mattson-100 was using a Mattson-100 apparatus.

Preparation of 3(N-glucidol-N-methyl)-2-hydroxypropyl methacrylate (GMHP)

9.75 g (50.0 mmol) of *N*-methyl-D-glucamine were dissolved in 30 mL of 2-methylpyrrolidone in a 250 mL flask, by heating at 50-60 °C for 20 min. During stirring 6.8 mL (50.0 mmol) of glycidyl methacrylate were added to the mixture. The stirring was continued at 60 °C for 4 h.

After the mixture was cooled off 150 mL of diethyl ether were dropwise added. The supernatant was decanted and 30 mL of ethanol added. The solution was added to 60 mL of ethyl acetate. The less heavy phase was seperated and ethyl acetate residues were removed using a rotary evaporator. A waxlike product was obtained in 84% (14.2 g) yield. All attempts to crystallize the product failed. The product was miscible with water, acetone, ethanol, NMP, DMF and immiscible with hydrocarbon solvents such as benzene, toluene, n-octane and diethyl ether.

The ¹H NMR and FT-IR spectra of this compound are given in Fig. 1 and Fig. 2, respectively.

N,N'-Tetraallylpiperazinium dichloride (TAP)

TAP was prepared according to a modified procedure of Biçak, as displayed in the following reaction scheme.



46 g (0.5 m) of piperazine were dissolved in 50 mL of methanol in a 500 mL-flask attached to a reflux condenser and dropping funnel. During stirring 82 mL (1 m) of allylchloride were added dropwise. Stirring was continued for 3 h at room temperature. A 1 m solution of KOH (56 g) in methanol was prepared and the half part added cautiously. After stirring for 3 h the remaining half of the KOH solution was added and stirred overnight. The stirring was stopped and the mixture was left to stand for 30 min for dismonuting the KCl. Then the suspension was filtered and the filtrate was transfered to a rotary evaporator. The methanol was removed and the liquid residue was transfered to a distillation flask. Distillation at 149-151 °C (1 mm Hg) leads to 62 g (74.7%) *N*,*N*'-diallylpiperazine (DAP) as colorless liquid.

50 g (0.3 m) of N,N'-diallylpiperazine and 49 mL (0.6 m) of diallyl chloride were placed in a closed bottle and left to stand for 20 days at room temperature. White crystalline precipitate of N,N'-tetraallylpiperazinium dichloride was filtered, washed with toluene and diethyl ether, and dried at 50 °C under vacumm for 24 h. The product was obtained in 50.6% yield (48 g) and exhibited a melting point between

211 and 213 °C. Since the melling point of TAP varies between 210 and 212 °C according to Buther and Ingley¹²), the results obtained here were in good agreement with the literature.

Preparation of crosslinked GMHP polymers

Two different approaches were followed in order to prepare crosslinked GMHP polymers. In the first approach (method A) N,N'-tetraallylpiperazinium dichloride was used as a crosslinking agent, whereas in the second approach (method B) no additional crosslinker was used. Instead a 10% excess of glycidyl methacrylate was used for the preparation of GMHP. The excess results in the formation of a diglycidyl derivative of *N*-methyl-D-glucamine which acts as crosslinker.

Method A

The monomer GMHP was prepared as described above. 15 g (44.5 mmol) of the monomer and 1.42 g of TAP (crosslinker) were dissolved in 40 mL of water that was distilled prior touse. This solution was transfered into a cylindirical glass reactor equipped with a mechanical stirrer and a nitrogen inlet. Under nitrogen atmosphere 200 mL of a toluene chloroform mixture (3:1) containing 0.2 of mL HLB 50 as stabilizer were added to the reactor. Additionally 0.4 g (1.5 mmol) of K₂S₂O₈ solved in 10 mL of water were added to the mixture. The nitrogen flow was stopped and the solution was stirred mechanically (\approx 400 rpm) at room temperature. After stirring the solution for 3 h the formation of solid particles began.

After stirring the solution for 5 h, the organic layer was decanted and 150 mL of acetone were added. The solid gel particles were filtered and left for 48 h in 100 mL of acetone at room temperature. The product was filtered, washed with ethanol (\approx 30 mL) and dried at 40 °C for 24 h under vacuumn. 12.8 g (78%) of dry GMHP were obtained.

Elementary microanalysis (calculated based on the feeding composition):

Method B

In a 250 mL flask 9.75 g (50 mmol) of *N*-methyl-D-glucamine and 7.5 mL (55 mmol) of glycidyl methacrylate were dissolved in 30 mL of 2-methyl pyrrolidone. The mixture was stirred and flushed with nitrogen. Then the flask was closed and heated at 70 °C until no turbidity was observed anymore, when adding few drops of the mixture to water, (approximately 6 h).

After the reaction was led to completion, the mixture was cooled to room temperature and 0.405 g (1.5 mmol) of $K_2S_2O_8$ dissolved in 30 mL of distilled water were added. The stirring was continued until gelation occured (≈ 4 h).

The clear gel formed was left overnight and then broken up and transfered into a heater containing 2 L of distilled water. The swollen gel was filtered and washed with an excess of water and with 50 mL of ethanol. The product was then dried at 50 $^{\circ}$ C in vacuum for 24 h and was obtained in 83% yield (14.6 g).

Elementary microanalysis (calculated based on the feeding composition):

Determination of the capacity for boron loading

In order to measure the capacity for boron loading, 1 g of the polymer samples were soaked into 20 ml of distilled water and left overnight. 60 mL of $0.2 \text{ M H}_3\text{BO}_3$ solution were added to these mixtures and stirred for 3 h at room temperature. The mixtures were filtered and 10 mL aliquots were transfered to 40 mL of 0.5 M d-sorbitol solution and titrated with 0.1 M NaOH solution in the presence of phenolphthalein indicator. The capacities were calculated from the differences in boron concentration of the initial and final concentrations of the boron solutions. The results are given in Tab. 1.

Kinetics of the trace boron sorption

In order to test boron sorption efficiency of the gel samples for trace quantities, the samples were interacted with H_3BO_3 solutions containing 41 ppm boron. Batch kinetic experiments were performed as follows:

0.5 g of dry gel were soaked into 20 mL of water and left overnight, in order to make sure that the equilibrium state of swelling was reached. Then 60 mL of H₃BO₃ solution (0.0041 M) were added reaching a boron concentration of 30.7 ppm. 5 mL of aliquots were taken and transfered to sample-bottles at appropriate time intervals using a filter paper. Boron contents of the solutions were determined colorimetrically ($\lambda = 585$ nm) using the carminic acid method¹³. Concentration-time plots of the solutions under investigation are given in Fig. 4.

Desorption of the boron from loaded gel samples

The boron-loaded polymer samples obtained from the capacity measurements were dried and 0.5 g of each sample were treated with 30 mL of a 1 M HCl solution for 24 h at room temperature and then filtered. Boron contents of the filtrates were measured colorimetrically using the carminic acid method. The results are given in Tab. 1.

The filtrated polymer samples were washed with an excess of water, treated for 30 min with 20 mL of a 0.1 M NaOH solution and washed again with an excess of water. Using this procedure the samples were almost boron-free and reusable for the next cycles.

In order to test the boron uptake activities of the regenerated samples, sorption-desorption experiments were repeated 4 times without measurements of the boron in the intermediate steps using 0.5 g of dry G2. Additionally, boron loading experiments were repeated, in order to see a change in the activity of boron sorption.

The results are shown in Tab. 1.

Polymer	$\frac{\text{Capacity}}{\text{mmol} \cdot g^{-1}}$	$\frac{\text{Theoretical capacity}^{a)}}{\text{mmol} \cdot g^{-1}}$	Desorbed boron ^{b)} 	Capacity after 5 times of regeneration
G1	2.12	2.72	2.10	2.13
G2	2.18	2.58	2.20	

Tab. 1. Boron sorption capacities of the gels

^{a)} Based on the feeding composition by assuming each mole of NMG binds 1 mol H₃BO₃.

^{b)} Based on dry boron loaded gels.

Results and discussion

Interaction of GMA with N-methyl-D-glucamine results in the formation of the corresponding macromonomer as displayed in Scheme 1. The reaction is mainly based on the ring opening of the oxirane by the amino group of NMG. The competitive reaction, Michael addition to the double bond, is slow compared to the ring opening reaction. The resulting macromonomer is a waxy product, which can be polymerized even after one month of storage at room temperature. The ¹H NMR spectrum (Fig. 1) of this compound confirms the proposed structure. The ratio of the integral of the methyl group of the methacrylate function at 1.9 ppm and of the hydroxy methyl groups from NMG, at 3.7 ppm is 4.3. The calculated ratio of these protons is 4. Similarly, the ratio of the integral of the olefinic protons and the methyl and methyl amine protons, respectively, is about 2.7. This result is in agreement with the expected value 2/7 = 0.285. The results obtained from elementary microanalysis also coincides with the predicted structure and implies therefore the absence of by-products carried by a Michael addition, since the Michael addition in connection with the ring opening of the epoxide would cause GMA/NMG will

Scheme 1:





Fig. 1. ¹H NMR spectrum of 3(*N*-glucidol-*N*-methyl)-2-hydroxypropyl methacrylate (GMHP)

lead to a ratio of 1:2. Here, the C/N molar ratio (from elemental analysis) would be 21/2 instead of 14/1 for the binding (1:1). Elemental analysis results confirm the estimated GMHP structure.

The salt of the macromonomer obtained from the reaction with HCl is the best way to stabilize the macromonomer. However, in the common organic solvents such as methanol, ethanol, acetone, etc., we were not able produce the salt of the macromonomer.

In the FT-IR spectrum of this compound (Fig. 2) the presence of C—H stretching vibration peaks of the olefinic group observed at 3050 cm⁻¹ is a qualitative evidence for the formation of GMHP. The disappearence of the characteristic epoxy group vibration at 1270 cm⁻¹ is a further indication for the ring opening reaction.

Crosslinking polymerization of the macromonomer

Two roots were followed for the crosslinking polymerization of the macromonomer as shown in Scheme 2. In the

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Fig. 2. FT-IR spectrum of 3(*N*-glucidol-*N*-methyl)-2-hydroxypropyl methacrylate (GMHP)

Scheme 2:



first one, tetraallylpiperazinium dichloride was used as crosslinker. The copolymerization was carried out at room temperature by the inverse suspension method using a mixture of toluene and $CHCl_3$ (3:1) as continous phase.

In the copolymerization we used $K_2S_2O_8$ alone (without tetramethyl ethylenediamine, TMED) for the redox initiation. Obviously, the secondary amine function of the monomer acts as a component of an amine-peroxide redox couple and forms radicals with potassium persulfate. The polymerization takes place at room temperature. However, this method leads to unperfect spherical beads. After drying the bead particles stick to each other, presumably, due to the strong hydrogen bonding between the hydroxy groups. In this study we did not focus on the production of perfect spheres.

In the second approach, no additional crosslinker was used. A 10% excess of GMA was used to form *N*-methyl-D-glucamine containing two methacrylate functions. The

Fig. 3. Swelling kinetics of the gels (G 1: •, G 2: •); W_0 and W are the dry and swollen weight of the samples

excess of GMA reacts with one of the OH groups of NMG and results in a bifunctional monomer which leads to crosslinking.

In situ polymerization of the mixture at room temperature in aqueous solution using exclusively $K_2S_2O_8$ leads to clear gels, as shown in Scheme 3.

Both gels exhibit moderate swelling as shown in Fig. 3. The two gels show equilibrium swelling about 4.5. This can be explained by the equal density of crosslinking (10%) of both gels. The swelling of G1 (containing quaternary amine) is faster compared to G2. Since the quaternary ammonium groups provide a high osmotic pressure in the micro domain of the gel.

This ionic effect can be deduced from the simple kinetic equation of Peppas¹⁾ ($w_t/w_{\infty} = k \cdot t^n$). The kinetic swelling data gives 0.55 for the exponent *n* of G1. Slight differences from 0.5 can be correlated with the effect of





the ionic groups in the gel. Whereas the gel G2 (without ionic groups) shows an average value for the exponent n of 0.5 which is consistent with the common behavior of the non-ionic gels¹⁴). In other words water diffussion into G2 obeys Fick's law.

Boron sorptions

In the boron uptake experiments buffer solutions were not used deliberately, since the application of buffer solutions is not an appropriate tool from the practical viewpoint, especially, when traces of boron have to be removed. Another important point is, that the presence of amino groups is essential for an efficient boron sorption. In that case, the proton liberated during the formation of the borate ester complex is captured by the amino group. Without the amino group the lower pH limit of carbohydrate-boron complexes is about 3 which implies 10⁻³ mol per liter boron complex. If the density of the gels in the swollen state were assumed to be about unity, this would come to 1 mmol boron per liter of swollen gel which is far more less than the theoretical capacity. As the complexation proceeds, boron is accumulated in the gel. This results in an increase in hydrogen ion concentration. Although the equilibrium in solution is not entirely conform with that one in the gel phase conditions, one can expect, that a higher proximity of complexing points will not be possible when the concentration of hydrogen ions in the micro domain is lowered. This results in an increase of unreacted chelating groups. So the net result must be low boron sorption. In the investigated case there is an amino group of N-methyl-D-glucamine present in the structure, and a high loading capacity boron towards can be achieved. Indeed, experimental results indicate that (Tab. 1) the capacities of both gels are high. The capacity of G1 is 2.12 mmol g⁻¹ and thus about 78% of the theoretical capacity that can be calculated from the feeding composition. Concerning G2, the observed capacity of boron loading is around 2.18 mmol g⁻¹ and thus 85% of the calculated capacity. The differences can presumably be explained due to the used crosslinker (N,N')tetraallylpriperazinium dichloride) containing quaternary ammonium groups. The attached cationic groups increase the osmotic pressure and may act as a preventive protection against the intrusion of boric acid inside the gel at least to some extent.

The kinetics of boron uptake from the solutions that contain 30.7 ppm of boron (Fig. 4), indicate a rapid binding of the boron by both gels. At a stirring rate of 400 rpm the boron concentrations of 80 mL solutions go down to almost zero within less than 15 min of contacting.

The gel containing a quaternary ammonium crosslinker is slow according to the adsorption of boron traces. In the kinetic experiments the pH remained constant. Since the sorption depends also on external factors such as stirring





Fig. 4. Concentration-time plots of 80 mL H_3BO_3 solutions (containing 30.7 ppm boron) interacted with 0.5 g dry gel (G 1: $\triangle,$ G 2: $\circ)$

rate, particle size and preparation conditions, we did not studied the kinetics systematically.

However, at the conditions studied, concentration-time plots displayed in Fig. 4, indicate a second order boron sorption with $k \approx 3.1 \text{ mol}^{-1} \text{ s}^{-1}$ for 0.5 g of gel. Hence, both gels are quite efficient for the removal of trace quantities of boric acid.

Regeneration of the gels

The gel samples loaded with boron were regenerated by decomplexation of the boron with 1 M HCl solutions. By the analyses of the boron concentrations of the acid solutions, the desorbed amounts were calculated and compared to those obtained by the loading experiments. Tab. 1 shows that the capacities found by loading experiments are almost equal to those obtained by the acid leaching (regeneration) experiments. On the other hand, boron sorption does not impart appreciable weight differences, since of the incorporation of one mol H_3BO_3 results in a weight increase of 61 g and is furthermore accompanied by the elimination of 3 molar of water which causes a decrease of the weight around 54 g.

So overall result is only 7 g of net weight difference since the average molecular weight of the repeating unit of G2 is 351.2, its 85% boron sorption capacity induces $0.85 \cdot 7 = 5.95$ g weight increase when taking into account this small difference, the capacity based on dry boron-free G2 is anounce 2.157 mmol \cdot g⁻¹. This capacity is almost equal to the capacity obtained from the loading experiment.

Similar correction for G1 results in loading capacity of 2.11 mmol \cdot g⁻¹. The slight deviation are within the error introduced from the experiment. The regeneration experiments indicate that 1 M HCl solution is able to dump all the complexed boron from the samples. In order to prove this assumption, the regenerated polymer samples were

Scheme 4:



filtered, washed with water and retreated with 10 mL of 1 M HCl solution. Here no boron was detected in the acid solution. This indicates a complete removal of sorbed boron by the first contact with 1 M HCl solution.

The boron free samples when treated with 0.1 M NaOH solutions for 30 min, the amino groups of the gels become HCl-free and ready for next cycles. In this study we have not investigated recyclability of the gels. However, in a preliminary investigation, G2 was loaded with boron and desorbed in turn as described above. Without measuring the capacities in the intermediate steps, after the fourth regeneration the regenerated gel was subjected to the boron loading. A capacity of 2.13 mmol • g⁻¹ was found indicating that nearly no activity loss was observed, at least, after the fifth regeneration. Of course, further studies are necessary to quantify the recyclabilities of the gels. However, the comparison of the investigated gels with chloromethylated polystyrene based polymer containing NMG functions⁹⁾ showed a low of activity of about 14%.

The gels presented here seem to be highly stable towards acid-base hydrolyses. The boron complexation with the gels and its decomplexation can be simply depicted as shown in Scheme 4.

The methacrylate ester backbone itself is known to be quite stable against hydrolysis. Since the other linkages are not sensitive towards hydrolysis the crosslinked polymers are expected to be recyclable many times without a loss of the boron uptake ability.

Due to the high boron uptake capacities and high efficiencies towards trace removal the gels presented (especially G2) may be of interest for the removal of boron from water in a large scale.

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