

6 Summary

Hydrogels are slightly cross-linked polymers which swell in water to a limited extent. Poly-2-hydroxyethyl methacrylate²⁾ (**Poly-HEMA**) takes up to about 38 % by weight of water. It shows outstanding mechanical properties, a very good transparency in visible light and good physiological compatibility. Therefore, it is used for the preparation of soft contact lenses. The drawback of this material is its relatively poor oxygen permeability $P_g = 8$ (ml $O_2 \cdot \text{cm}^2 / \text{ml} \cdot \text{s} \cdot \text{mmHg}$).

In this thesis the following cross-linkers have been used:

1. ethylene dimethacrylate **EGDMA (1)**
2. 2-butin-1,4-ylen-dioxy methacrylate **B-DMA (2)**
3. 2,2-bis-(methacryloyloxyphen-4-ylen)propane **Bis-MA-O-Ph-P (3)**
4. 1,4-bis-(methacryloyloxy-4-benzoyloxy)benzole **Bis-MA-O-B-O-B (4)**

We hoped that the cross-linkers **2**, **3** and **4** produce a broad-mesh network by increasing the water content. These cross-linkers compared to cross-linker **1** do not show any increase in the water content and oxygen permeability for the hydrogels. These results indicate that the expected hollows do not form. By increasing the number of cross-linkers, the water content, the linear expansion and oxygen permeability reduce and the values of the extractables increase, because a part of the cross-linkers do not polymerize. For the following reasons the produced hydrogels are synthesized by using cross-linker **1 (EGDMA)** and azo-bis-isobutyronitrile (**AIBN**) as an initiator.

If one substitutes a part of HEMA by acrylamid (20 – 50 mol %) we notice an increase in the water content, oxygen permeability, linear expansion and values of extractables (see hydrogels 1 – 74). Here too the increase in the number of cross-linkser, like described above, decreases the water content, linear expansion and oxygen permeability, and increases the values of extractables (see Chap. 3.5).

For the synthesis of superhydrophilics and superhydrophobics we have used the following monomers:

Hydrophilic components:

5-O-crotonyl-di-O-isopropylidene-adonitol **5-CDP-Ado (41)**, 5-O-crotonyl-di-O-isopropylidene-xylitol **5-CDP-Xy (42)**, 5-O-methacryloyl-di-O-isopropylidene-adonitol **5-MDP-Ado (43)**, 5-O-methacryloyl-di-O-isopropylidene-xylitol **5-MDP-Xy (44)**, 1-O-methacryloyl-1,2;4,5-di-O-isopropylidene- β -D-fructopyranose **1-MDP-Fru (45)**, 3-O-methacryloyl-1,2;4,5-di-O-isopropylidene- β -D-fructopyranose **3-MDP-Fru (36)**, 3-O-crotonyl-1,2;4,5-di-O-isopropylidene- β -D-fructopyranose) **3-CDP-Fru (46)**, 6-O-acryloyl-1,2;4,5-di-O-isopropylidene- α -D-galactose **6-ADP-Gal (40)**, 6-O-methacryloyl-1,2;4,5-di-O-isopropylidene- α -D-galactose **6-MDP-Gal (48)**, 6-O-crotonyl-1,2;4,5-di-O-isopropylidene- α -D-galactose **6-CDP-Gal (49)**, 2-hydroxyethyl methacrylate **HEMA (5)**, N-Vinyl-pyrrolidine **NVP (8)**

Hydrophobic components:

Methylmethacrylate **MAA (50)**, 2-(trimethylsilyloxy)ethyl methacrylate **tm-Si-O-EMA (51)**, 2,2,3,3-tetrafluoropropyl methacrylate **TF-p-MA (52)**, hexafluoroisopropyl methacrylate **HF-ip-MA (53)**, 2,2,3,3,4,4,4-heptafluorobutyl methacrylate **HF-Bu-MA (54)**, 3-methacryloxypropyl-tris(trimethylsilyloxy)silane **MA-p-Ts-TSi (55)**, 1,3-bis-(3-methacryloxypropyl)-tetrakis(trimethylsilyloxy)disiloxane **DMA-p-Ts-TSi (56)**

Because of the incompatibility between hydrophilic and hydrophobic monomers we use protective groups (isopropylidene protective groups) to hydrophobize the polyalcohols (see Chap. 3.8.1). The Grunenberger-method offers not only an easier preparation but also higher results eg. **5-DP-Xy (17)** after distillation 67 % o. th. (isomeric mix). After the **first distillation** and crystallisation from hexane we get 53 % of pure isomer (see Chap. 4.2.4). Contrary to this, we get with other methods and time-consuming distillations, pure isomer⁶⁾ only after the 16. fraction. Subsequently, we have achieved great progress ecologically and economically in the synthesis of pure isomers **5-DP-Xy (17)**.

Protected polyalcohols in the form of sugar-carbonates are not suitable for the polymerization with other monomers (see Chap. 3.10.1.1) except for **MDC-Fru (28)** which later, however, recrystallizes into polymermatrix. Sugarboronates are also not polymerisable. The purification and isolation of hexoseboronate and pentoseboronate are not possible (see Chap. 3.10.2.1).

Synthesis of all the polymerisable monomers all are well-known except for adonitol-derivative. Synthesis using method III (the use of catalysor **4-DMAP (47)** (see Chap. 3.11)) proved the best.

The oxygen permeability in the case of hydrogels increases through the influence of hydroxygroups (polyalcohol), which leads to the increase of water-content. The hard contact lenses attain their stability through monomers like **MMA (50)** and perfluoroalkyl methacrylate – the latter increases oxygen permeability. Therefore, for the synthesis of hydrophilic-hydrophobic hydrogels the combination of above mentioned hydrophilic monomers and some selected perfluoroalkyl methacrylates, **TF-p-MA (52)**, **HF-ip-MA (53)** and **HF-Bu-MA (54)** are used. The results show that it is possible (see Chap. 3.12 – 3.15) that hydrophobic components like **MMA (50)** increase the stability (see Chap. 3.14.3) and perfluoroalkyl methacrylate with comonomers increase the oxygen permeability.

The expected rising water content of these hydrogels is observed after splitting off the protective groups (see Chap. 3.12.2.3.1, 3.12.2.5.2, 3.12.2.7 and 3.15 and also Chap./Diag. 3.14.3.3 / 69, 3.15.1.3 / 73, 3.16.1.4 / 78, 3.16.3.4 / 83). The oxygen permeability of the unsplit (hydrated) hydrogels are determined by the perfluorinated methacrylates **TF-p-MA (52)**, **HF-ip-MA (53)** and **HF-Bu-MA (54)**. On the other hand, the O₂-permeability of the hydrolyzed hydrogels rises through rehydrophilysed sugar alcohols and the influence of perfluorinated methacrylates (see Chap. 3.12.2.1 – 3.15.1 and 3.17).

The O₂-permeability diagramme of these hydrogels has the form of a parabel. The left side shows the influence of **TF-p-MA (52)**, **HF-ip-MA (53)** and **HF-Bu-MA (54)** and the right side shows the influence of polyalcohols (see Chap./Diag. 3.12.2.5.6 / 40, 3.14.1.5 / 60, 3.15.1.4 / 74, 3.17 / 89). A further proof is given by the hydrogels **5-MDP-Xy (17)** and **MMA (50)**: since there are no perfluorinated methacrylates we see only a rising tendency of O₂-permeability with successive rising parts of polyalcohols **5-MDP-Xy (17)** (see Chap. /Diag. 3.14.3.4 / 70). The hydrogels made of galactose **6-MDP-Gal (48)** do not show any positive results (see Chap. 3.13). The conditions for splitting off the protective groups need to be changed to prove a difference between hydrolyzed and hydrated polymers (see Chap. 3.13.1 – 3.13.2.5).

All produced and examined hydrogels made of sugar alcohols and perfluorinated methacrylates were unknown with the exception of saccharide methacrylates **HF-Bu-MA (54)** and **MMA (50)**. The hydrogels made of sugar alcohols **5-MDP-Ado (43)** and **5-MDP-Xy (44)** with **HEMA (5)** and with perfluorinated methacrylates **TF-p-MA (52)**, **HF-ip-MA (53)** and **HF-Bu-MA (54)** and **MMA (50)** show very good results. They are easy to hydrolyse and have good attributes for contact lenses, with high water content, high O₂-permeability [40 (ml O₂ * cm²/ ml * s * mmHg)], limited linear expansion, low extractables and good mechanical and optical attributes.

Superhydrophilic polymers also with perfluorinated methacrylate comonomers distributed in the molecular scale (without phase separation) also have high water contents, high oxygen permeabilities and still better mechanical stabilities. With increasing contents of the perfluorinated methacrylate comonomer an increase in mechanical stability has been found (ball indentation hardness up to 175 N / mm² after 60 s). Extractables are between 0,20 to 16,0 % by weight. Our superhydrophilic saccharide acrylate and methacrylate polymers contain high water content, flexibility, good mechanical stability and high oxygen permeabilities

The hydrogels 239 – 260 (see Chap. 3.16) with parts of siloxane **MA-p-Ts-TSi (55)** and 1,5 mol % cross-linker **DMA-p-Ts-TSi (56)** with the sugar alcohols **5-MDP-Xy (44)**, **3-MDP-Fru (36)** and **HF-ip-MA (53)** are compatible, have a good refractive index n_D^{35} (1,336 – 1,430), good water-reception, an exceptionally high O₂-permeability compared to hydrogels made of **1-MDP-Fru (45)** or **3-MDP-Fru (36)** / **HF-ip-MA (53)** (O₂-permeability 20 – 58, see Chap. 3.12.2.4 – 6, Tab. 21 and 26). **5-MDP-Xy (44)** / **HF-ip-MA (53)** have an O₂-permeability of 20 – 44 (see Chap. 3.16.1, Tab. 43 – 46).

These hydrogels with their sugar alcohols and perfluorinated methacrylates due to a chemical interaction lead to a phase shift, rise of bulb structures and formation of hydrophilic / hydrophobic domains (see Chap. 3.8). Microspaces are formed in the hydrogels which lead to a high water absorbtion and subsequently an increase in the

oxygen permeability (see Diagram 88 - 89). This phenomenon has been proved through a thermomechanical analysis (TMA) with the help of some measured glass transition temperatures (TG) of the polymers HEMA / Xylit HF-Bu-MA (60°C and 120°C) as well as HEMA / Xylit HF-iP-MA (75°C and 120°C). For these reasons the hydrogels made up of sugar alcohols, siloxane and perfluorinated methacrylates are a good solution for contact-lens materials because they are flexible, have a good water content and an exceptionally high oxygen permeability.