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The use of *N,N′*-diallylaldardiamides as cross-linkers in xylan derivatives-based hydrogels

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ABSTRACT

N,N′-Diallylaldardiamides (DA) were synthesized from galactaric, xylaric, and arabinaric acids, and used as cross-linkers together with xylan (X) derivatives to create new bio-based hydrogels. Birch pulp extracted xylan was derivatized to different degrees of substitution of 1-allyloxy-2-hydroxy-propyl (A) groups combined with 1-butyloxy-2-hydroxy-propyl (B) and/or hydroxypropyl (HP) groups. The hydrogels were prepared in water solution by UV induced free-radical cross-linking polymerization of derivatized xylan polymers without DA cross-linker (xylan derivative hydrogel) or in the presence of 1 or 5 wt % of DA cross-linker (DA hydrogel). Commercially available cross-linker (+)-*N,N′*-diallyltartardiamide (DAT) was also used. The degree of substitution (DS) of A, B, and HP groups in xylan derivatives was analyzed according to ^{1}H NMR spectra. The DS values for the cross-linkable A groups of the derivatized xylans were 0.4 (HPX-A), 0.2 (HPX-BA), and 0.4 (X-BA). The hydrogels were examined with FT-IR and elemental analysis which proved the cross-linking successful. Water absorption of the hydrogels was examined in deionized water. Swelling degrees up to 350% were observed. The swollen morphology of the hydrogels was assessed by scanning electron microscopy (SEM). The presence of cross-linkers in DA hydrogels had only a small impact on the water absorbency when compared to xylan derivative hydrogels but a more uniform pore structure was achieved.

1. Introduction

Hydrogels are chemically or physically cross-linked networks that are water-insoluble but capable of absorbing large amounts of water.[1] They can be made of synthetic or natural starting materials but commercial hydrogels have traditionally been prepared mainly from toxic acrylates and acrylamides.[2] Hydrogels based on naturally occurring products are of interest not only for their renewable character and nontoxic nature but because they may offer biocompatibility and biodegradability. Hydrogels possess a degree of flexibility due to their significant water content and they are potential material candidates, for example, in tissue engineering,[3] controlled drug release,[4,5] agriculture,[6,7] and hygiene products.[8] Especially beneficial for future applications is the obvious biodegradability of polysaccharide and aldaric acid based materials.

Carbohydrates are a class of natural products that are widely available in nature. They have a wide range of functionalities and are very hydrophilic, which makes them good candidates for hydrogel preparation. Hemicelluloses, such as xylan, have hydroxyl groups in each repeating unit that can be chemically derivatized to new reacting groups. When compared with cellulose and starch, hemicelluloses have been somewhat neglected in research and they are normally disposed of as organic waste from the forest industry sidestreams. However, recent research has begun to find new applications for hemicelluloses and examples of hydrogels prepared from modified hemicelluloses can be found.[9–13]

Hemicelluloses can also be hydrolyzed to monosaccharides to obtain, for example, xylose, arabinose, galactose, and mannose that can be oxidized to aldaric acids. Aldaric acids are typically prepared by simple chemical oxidations of sugars, but can also be produced biotechnically.[14] These diacids can be used as starting materials, for example, in the preparation of diallyl functionalized cross-linkers or other derivatives.[15] The aim of this work was to synthesize analogues of the commercially available cross-linker (+)-*N,N′*-diallyltartardiamide (DAT) and further use them as novel cross-linkers in the preparation of bio-based hydrogels. Some syntheses of *N,N′*-diallylaldardiamides (DA) have been described in the literature but none starting with bio-based starting materials or used in cross-linking reactions. Anker[16] has reported the preparation of polyacrylamide gels using DAT as a cross-linker instead of the normally used methylenebisacrylamide (MBA). Two references of *N,N′*-diallylgalactardiamide (DAG)[17,18] and one of *N,N′*-diallylxylardiamide (DAX)[17] were found. In contrast, no references for *N,N′*-diallylarabinardiamide (DAA) were found in the literature so far.

We report here novel xylan based hydrogels prepared in water solution by cross-linking xylan derived polymers with and without *N,N′*-diallylaldardiamide cross-linkers. Three different xylan

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derivatives were prepared: HPX-A, HPX-BA, and X-BA. HPX-A and HPX-BA were prepared from xylan by first attaching hydroxypropyl (HP), and subsequently 1-allyloxy-2-hydroxy-propyl (A) or both 1-allyloxy-2-hydroxy-propyl (A) and 1-butyloxy-2-hydroxy-propyl (B) groups, respectively. X-BA was prepared from xylan by attaching directly A and B groups to the xylan backbone. 1-Allyloxy-2-hydroxy-propyl (A) group is a cross-linkable allyl functionality which was used as the cross-linking site in this research. Polysaccharides have previously been derivatized with similar groups, for example, Huijbrechts et al.[19] have modified starch with allyl glycidyl ether and compared its physicochemical properties compared to native starch. Shen et al.[20] have modified carboxymethyl cellulose to obtain an allyl functionalized derivative, *N*-allylcarbamoylmethyl cellulose, for hydrogel preparation. We chose aldaric acid based cross-linkers not only because they are bio-based but because this permits cross-linking reaction in water. Derivatized xylan was cross-linked without DA cross-linker as well as with four different types of cross-linkers (DAT, DAX, DAA, and DAG). The morphological and swelling properties of the hydrogels were determined.

2. Results and discussion

2.1. Synthesis of xylan hydrogels

Three different cross-linkers, DAX, DAA, and DAG, were synthesized from aldaric acids. Commercially available cross-linker (+)-*N,N′*-diallyltartardiamide (DAT) was also used. The reaction route for the synthesis of the cross-linkers is shown schematically in Scheme 1. Xylaric (**1a**) and arabinaric (**1b**) acids were synthesized according to the literature[21] from xylose and arabinose, respectively. Galactaric acid (**1c**) was commercially available. All the diacids were esterified[22] with methanol to the corresponding diesters (**2a**, **2b,** and **2c**) and subsequently reacted with allylamine[16] in dry tetrahydrofuran to obtain white crystalline cross-linkers DAX (**3a**), DAA (**3b**), and DAG (**3c**). The yield of **3c** (59%) was better than the yields of **3a** (37%) and **3b** (32%). This can be due to the fact that the starting materials for the reaction with allylamine, **2a** and **2b**, were syrupy products with some solvent or other small molecule impurities and were used in the synthesis as such with no additional purification steps.

All cross-linkers were verified by ^{1}H NMR. A representative ^{1}H NMR spectrum of a DA cross-linker (DAG) is shown in Figure 1. The cross-linkers were soluble in DMSO and water. No peaks are seen from methyl ester which indicates a successful reaction with allylamine. The amide proton gives a peak at 7.73 ppm and the double bond gives peaks at 5.84 and 5.14 ppm. The methylene protons next to the amide group can be seen at 3.78 ppm.

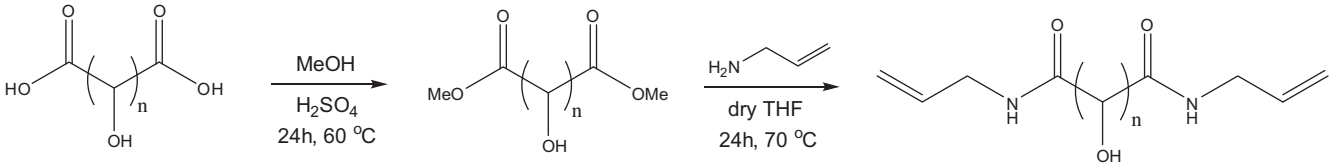
Non-dried (5–11 wt % of xylan, containing 0.9% NaOH) or dried xylans extracted, for example, from bleached birch pulp[23,24] were used as starting materials in the preparation of hydrogels. Xylan polymer repeating unit has two secondary hydroxyl groups, which can be derivatized to different DS-values with varying derivatizing agents. Hydroxypropylation increases the hydrophilicity of xylan thus improving the solubility of xylan to water.[25] Hydroxypropylation of xylan was performed according to the literature.[25] Hydroxypropylated or unmodified xylan was reacted in alkaline conditions with allyl glycidyl ether and/or butyl glycidyl ether to obtain three different xylan derivatives (HPX-BA, HPX-A, and X-BA) with different structures and DS-values of allyl groups and other substituents (Figs. 2–4). 1-Allyloxy-2-hydroxy-propyl (A) group is a cross-linkable functionality. In addition, the A and 1-butyloxy-2-hydroxy-propyl (B) groups form a similar structure compared to free HP groups with a secondary hydroxyl group in carbon-2 thus also improving the water solubility. X-BA prepared from unmodified xylan without hydroxypropylation had a similar water solubility compared with HPX-BA and HPX-A. All the xylan derivatives were soluble into water up to 15–20 wt %. The effect of the non-reacting B group similar in size to A group in hydrogels was studied to investigate the reactivity differences and water absorption capacities. The DS-values of the xylan derivatives were determined by the integration of ^{1}H NMR spectra.[26] In addition, DS-values of allyl groups were verified using a bromination method. DS-values are presented in Table 2.

The hydrogels were prepared by cross-linking the xylan derivatives without the DA cross-linker or by inserting the DA cross-linker between the xylan polymer chains. When no additional DA cross-linker is present the cross-linking reaction takes place between the A groups of the modified xylan polymers. The cross-linking was done in a 10% water solution of the xylan polymer. The derivatized xylan polymers dissolved well in water and the obtained solutions were slightly cloudy. The cross-linkers were dissolved in water prior to mixing with the polymer solution. Potassium persulfate was used as the photoinitiator and it was dissolved in a small amount of water prior to mixing with the solution of xylan polymer and the cross-linker. Samples were put on Petri dishes and exposed to UV light in an UV oven. The samples were irradiated in 30 s periods and let to cool down in between. The gels were irradiated for 3–4 min (Fig. 5).

2.2. Characterization

A representative FT-IR spectra of a derivatized xylan hydrogel prepared with no additional DA cross-linker (red spectrum) and the DA cross-linked hydrogel (black spectrum) are shown in Figure 6. The spectra were quite similar since the only new functional group introduced by the cross-linking reaction with DA cross-linkers was the amide group. A differing amide peak was seen at 1538 cm^{-1} (black spectrum).

DA hydrogels were analyzed for their nitrogen content to investigate the reactivity and incorporation of the DA cross-linkers into the hydrogel network. The DA cross-linkers contain an amide group allowing elemental analysis as a means to prove the incorporation of the cross-linkers in between the derivatized xylan



1a: (n=3) Xylaric acid
1b: (n=3) Arabinaric acid
1c: (n=4) Galactaric acid

2a: (n=3) Dimethyl xylarate
2b: (n=3) Dimethyl arabinarate
2c: (n=4) Dimethyl galactarate

3a: (n=3) DAX
3b: (n=3) DAA
3c: (n=4) DAG
3d: (n=2) DAT

Scheme 1. A schematic representation of the preparation of DA cross-linkers.

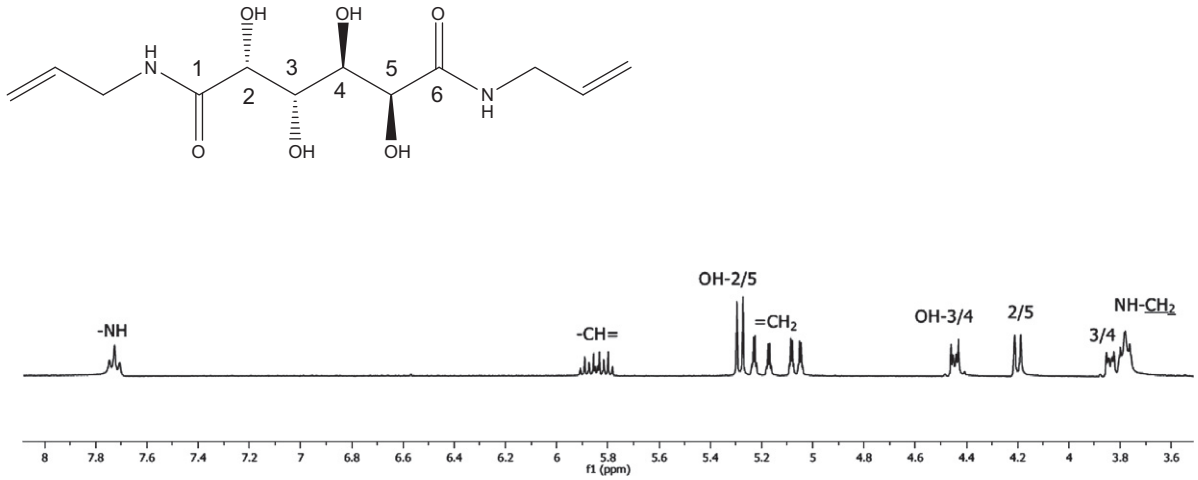


Figure 1. ^{1}H NMR spectrum of DAG recorded in DMSO-d_6.

chains. Varying amounts of nitrogen were found. Differences in nitrogen contents may be due to reactivity differences of the DA cross-linkers. The elemental analysis for the samples cross-linked with 5 wt % of cross-linker gave increased values of nitrogen, a clear indication of a successful cross-linking reaction. The incorporation efficiency for all of the DA cross-linkers was calculated from the elemental analysis results as shown in Table 1. The incorporation efficiencies of DAA, DAX, and DAG cross-linkers are comparable to the results of the commercially available cross-linker DAT. X-BA hydrogels seem to have the lowest and HPX-A hydrogels the highest incorporation efficiency of DA cross-linkers. The higher incorporation efficiency of DA cross-linkers into HPX-A hydrogels can be due to the fact that there are no interfering butyl groups during the cross-linking reaction thus allowing the allylic double bonds to react more freely and also due to lower cross-linking efficiency of allylic double bonds among themselves (see Table 2). The results from the elemental analysis for the samples with 1 wt % of cross-linker were below detection limit and therefore could not be reliably interpreted.

The incorporation of the DA cross-linkers was also apparent from the transparency of the hydrogels: the gel with 5 wt % of cross-linker (left) was whiter and almost opaque whereas the gel with 1 wt % of cross-linker (right) was semi-opaque (Fig. 7). The gels with no additional cross-linker were almost completely transparent (data not shown).

The cross-linking efficiency of allyl functionalities in the xylan derivatives without DA cross-linkers was demonstrated using a bromination method of allylic double bonds with bromine.[27] Table 2 shows the bromine content of the analyzed xylan derivatives. As xylan does not contain double bonds, it was used as the reference sample and accordingly no bromine was found. When comparing the starting material HPX-A to the cross-linked HPX-A, a decrease in the amount of bromine from 13.7 wt % to 11.3 wt % was seen, which indicates that double bonds have reacted. The cross-linking efficiency was calculated to be 18%. Similarly, the bromine content was observed to decrease from 6.5 wt % of HPX-BA to 4.4 wt% of the cross-linked HPX-BA, and from 10.9 wt % of X-BA to 5.4 wt % of the cross-linked X-BA. The cross-linking efficiencies were 32% and 50%, respectively. Allylic double bonds of X-BA seem to cross-link best among themselves leading to a less efficient incorporation of the DA cross-linkers into the hydrogel network. In conclusion, when the cross-linking efficiency of the allyl functionalities among themselves is lower, the incorporation of the DA cross-linkers is higher (see Tables 1 and 2).

DS-values of allylic double bonds were calculated using the bromination method taking into account the amounts of other substituents in a xylan derivative.[26,27] DS-values of other substituents (B and HP) were calculated from ^{1}H NMR measurements. DS-values using the bromination method were slightly lower than DS-values calculated from ^{1}H NMR measurements as observed previously by Lepistö et al.[28] The reason may be that the bromination reaction is not quantitative and/or ^{1}H NMR measurement gives too high DS-values. However, the two methods gave comparable results.

SEM was used to characterize the morphology and structural differences between the derivatized xylan hydrogels and the DA hydrogels. The hydrogel samples were immersed in liquid nitrogen and freeze-dried before the SEM analysis. Typical images of the derivatized xylan hydrogels and the DA hydrogels are presented in Figures 8 and 9, respectively. The hydrogels with DA cross-linkers clearly had a more uniform and even pore structure as compared to the derivatized xylan hydrogels with no additional cross-linkers. The same pattern in the morphology could be observed for all the hydrogels.

2.3. Swelling measurements

Swelling measurements were performed for all synthesized hydrogels by placing the dried gels in an excess of deionized water at room temperature. Figure 10 shows the differences in absorbencies between the derivatized xylan hydrogels (X-BA, HPX-BA, and HPX-A) with no additional cross-linkers. It was expected that the gels made with xylan derived polymer with the lowest DS of cross-linkable allyl groups (0.2 for HPX-BA) would have the loosest network of cross-links and thus the highest water absorbency. However, water absorbency was highest for HPX-A and the lowest for X-BA both of which have a DS of allyl groups 0.4 based on the NMR measurements. According to cross-linking efficiencies, X-BA and HPX-BA form a more dense network and thus absorb less water than HPX-A, a similar phenomenon observed by Voepel et al.[29] when preparing *O*-acetyl galactoglucomannan hydrogels. The lower water absorbency can also be due to the presence of butyl groups in HPX-BA and X-BA polymers that makes them more hydrophobic. This is in accordance with previous work done with xylans where the water absorbency decreased after bringing hydrophobic groups to the xylan backbone.[13] The hydroxypropyl groups in the xylan backbone of HPX-A and HPX-BA also seemed to have a positive influence on the water absorption due to longer side chains enabling a more open structure.

Hydrogels with DA cross-linkers showed the same swelling trend than the hydrogels with no additional cross-linker. The amount (1 or 5 wt %) and type of DA cross-linker used had some

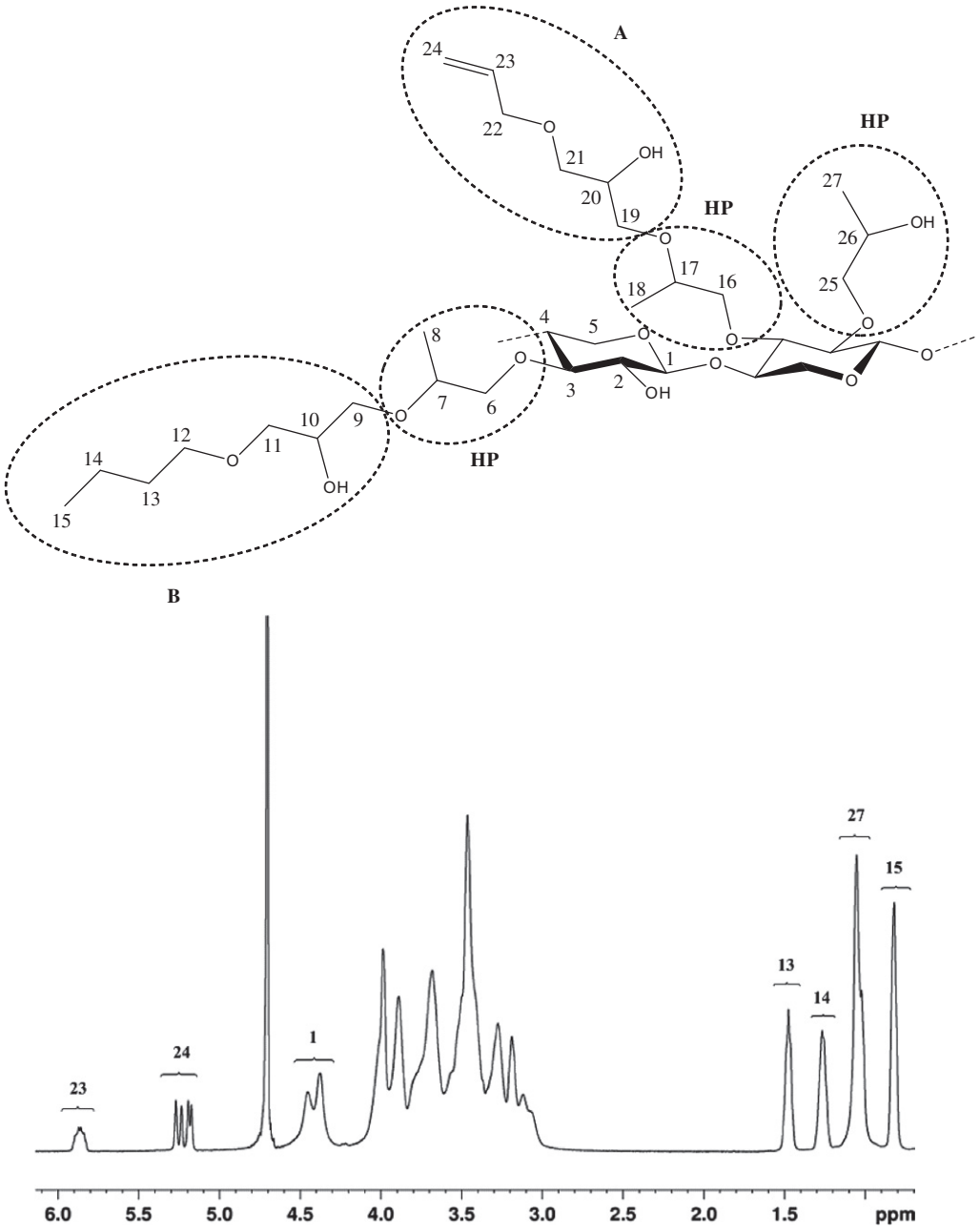


Figure 2. [1]H NMR spectrum of HPX-BA.

influence on the water absorbency (Fig. 11). A general trend for hydrogels prepared from X-BA was observed: the gels prepared with 5 wt % of any DA cross-linker absorbed less water than those prepared with 1 wt % cross-linker. This could be due to the higher density of the network in the gels prepared with 5 wt % cross-linker and could be expected also for the other hydrogels.[30] However, the hydrogels prepared with HPX-A showed no significant differences in the absorbencies between gels prepared with 1 or 5 wt % of any DA cross-linker. Only the HPX-A hydrogel cross-linked with DAX showed a similar swelling behavior than the X-BA hydrogels. HPX-BA hydrogels had varying swelling properties. The gels cross-linked with 1 or 5 wt % of DAG or DAX had no significant differences in swelling properties, whereas the gels cross-linked with 5 wt % of DAT absorbed more water than the gels cross-linked with 1 wt % of DAT. The gels cross-linked with DAA showed the opposite effect.

3. Experimental

3.1. Materials

The following reagents were used as received: (+)-*N*,*N*′-diallyltartardiamide (99+%, Aldrich), D-(+)-xylose (⩾99%, Sigma–Aldrich), L-(+)-arabinose (99%, Sigma), galactaric acid (mucic acid, 97%, Aldrich), allylamine (⩾98.0%, Fluka), tetrahydrofuran (99.9%, Aldrich), methanol (HPLC grade, Rathburn), ethanol (Ba, Altia), sulfuric acid (95–97%, Fluka), nitric acid (⩾65%, Fluka), 2-propanol (HPLC grade, Rathburn), allyl glycidyl ether (⩾99%, Sigma–Aldrich), butyl glycidyl ether (95% Aldrich), propylene oxide (99%, Sigma–Aldrich), NaOH (30% w/w, Reagecon), HCl (37%, Sigma–Aldrich), acetone (technical grade, YA-kemia), *t*-BuOH (>99.0%, Fluka). The following starting materials were synthesized according to literature: hydroxypropylated xylan,[25] dimethylgalactarate, dimethylxylarate

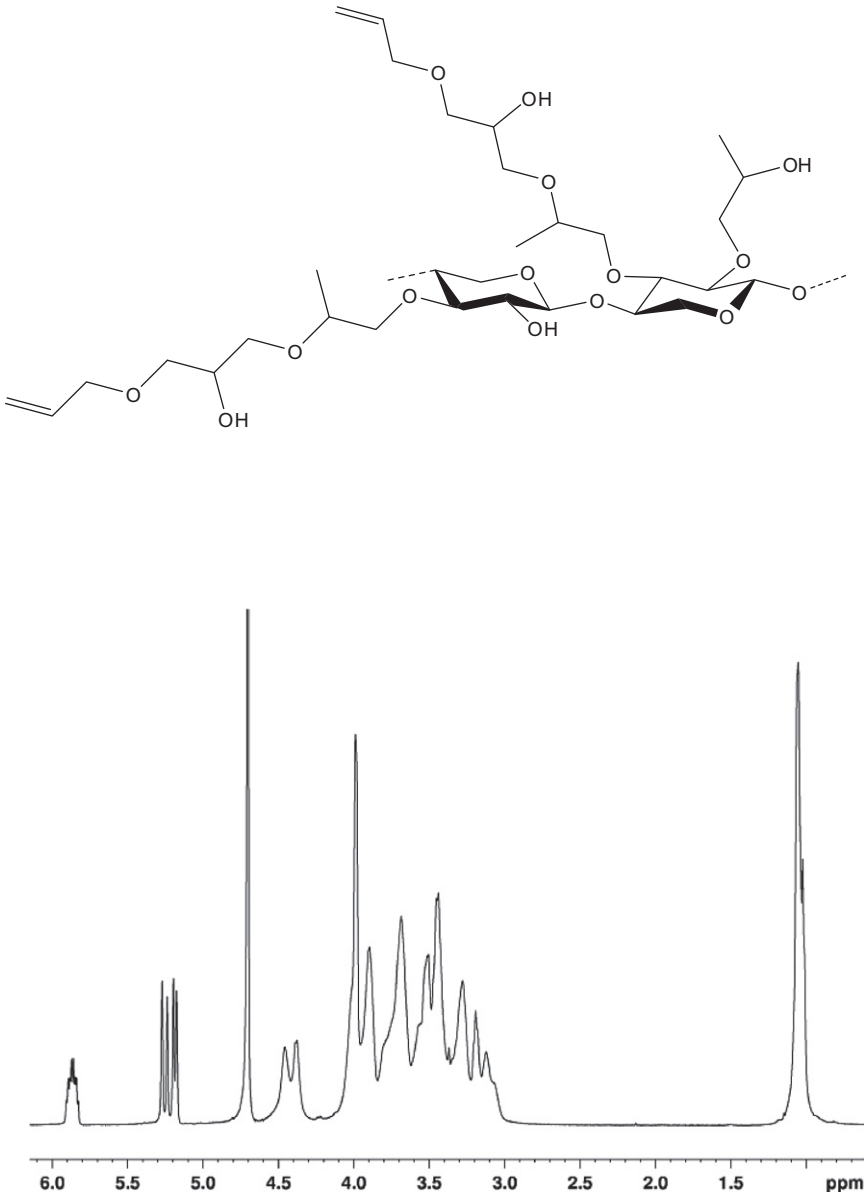


Figure 3. ^{1}H NMR spectrum of HPX-A.

and dimethylarabinarate,[22] and xylaric and arabinaric acid.[21] The cross-linkers were prepared according to Anker.[16] All the cross-linkers were soluble to water but the dissolution of DAG required some heating. Never-dried (5–11 wt % of xylan, containing 0.9% NaOH) or dried xylans extracted, for example, from (bleached) birch pulp were used as starting materials in the preparation of hydrogels.

3.2. Methods

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury VX (300 MHz) spectrometer or on a Bruker Avance III (500 MHz) spectrometer in DMSO or D_2O. Melting points (mp) were determined in open capillaries using SANYO Gallenkamp mp apparatus. Elemental analyses were performed on Elementar Analysensysteme GmbH Variomax CHN analyzer. Bromine samples were irradiated in the TRIGA MARK II reactor followed by analysis with an automatic HPGe-detector attached to an automatic gamma spectrometer. The accuracy of the bromination method is ±10%. IR spectra were recorded on a Bruker Equinox 55 FTIR spectrometer. Mass spectra were recorded using direct infusion ESI technique on MicroMass Quattro II Spectrometer. An F300S UV system (Fusion UV Systems, Inc.) was used for the irradiation of the hydrogel samples. The UV system consists of a P300MT power supply and an I300MB irradiator which emits UV light in a range from 200 to 400 nm. The structures of the swollen gels were characterized by SEM (LEO DSM 982 Gemini FEG-SEM).

3.3. Synthesis of the monomers

3.3.1. *N,N′*-Diallylarabinardiamide (3b)

L-(+)-Arabinose was oxidized[21] to L-(+)-arabinaric acid (**1b**) with concentrated HNO_3 and subsequently esterified[22] with methanol according to Kiely et al. The resulting syrupy dimethylarabinarate **2b** (21.9 g, 0.105 mol) was dissolved under argon in dry tetrahydrofuran (210 mL) in 500 mL glass flask. Allylamine (24.5 mL, 0.326 mol) was added and the temperature was raised to 70 °C. After 22 h the solution was cooled and the crystals were filtered and washed with THF/10% ethanol-solution (110 mL). Light yellow crystals were obtained, yield 8.6 g (32%): mp 180–185 °C; IR: *ν* 3280 (amide I), 3082 (CH=), 1638 (CO), 1553 (amide II), 1045

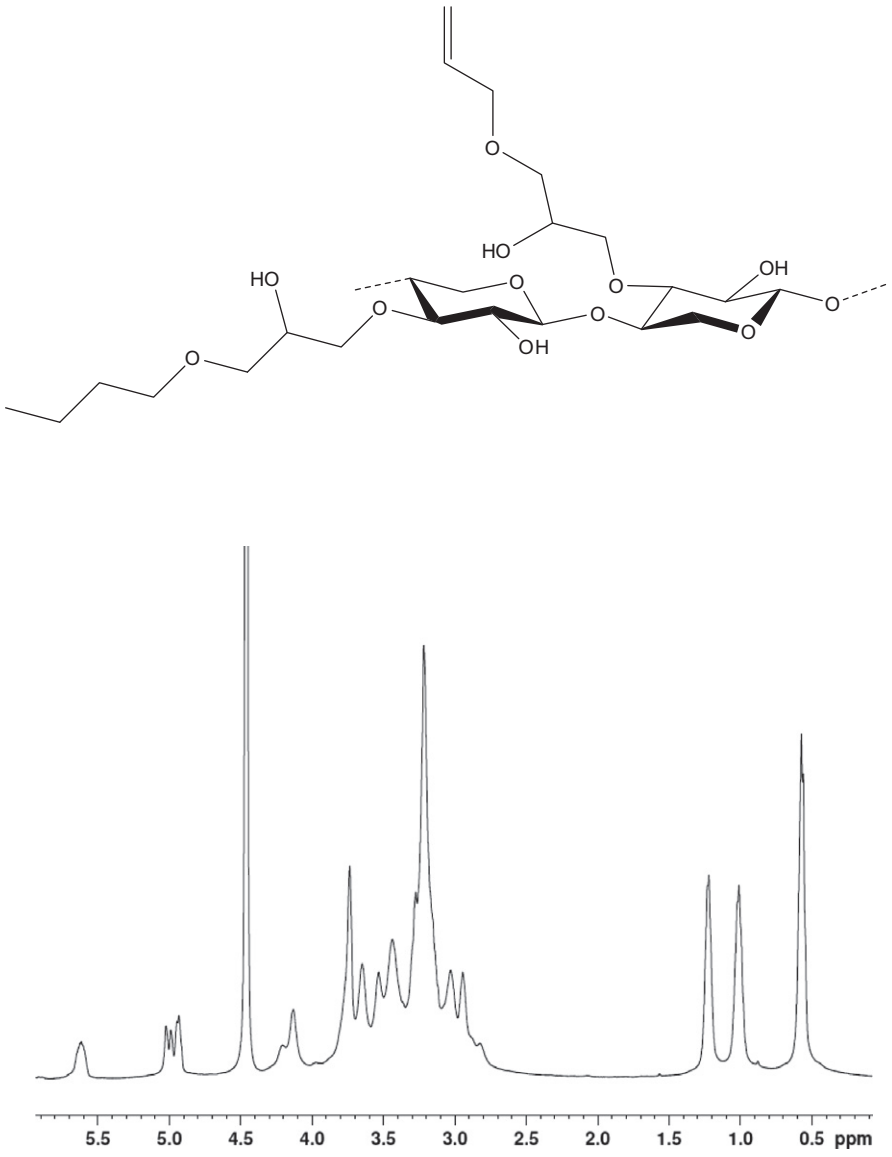


Figure 4. ^{1}H NMR spectrum of X-BA.

(OH) cm^{-1}. ^{1}H NMR (Me_2SO-d_6, 300 MHz): δ 8.10 (t, 1H, NH, J = 11.4 Hz, J = 6.0 Hz), 7.76 (t, 1H, NH, J = 6.1 Hz, J = 12.5 Hz), 5.82 (m, 2H, allyl =CH, J = 1.8 Hz), 5.62 (d, 2H, OH-2/4, J = 6.2 Hz), 5.12 (m, 4H, allyl CH_2=, J = 1.8 Hz), 4.77 (d, 1H, OH-3, J = 6.3 Hz), 4.15 (dd, 2H, H-3, J = 1.5 Hz, J = 6.1 Hz), 3.95 (m, 2H, H-2/4, J = 1.5 Hz, J = 6.3 Hz), 3.77 (t, 4H, –CH_2–NH, J = 5.5 Hz); ^{13}C NMR (Me_2SO-d_6, 75 MHz): 174.2, 173.3 (CONH), 136.3, 136.0 (–CH=CH_2), 116.0, 115.8 (–CH=CH_2), 73.9 (C-3), 72.4, 72.3 (C-2 ja C-4), 41.6 (CH_2–NH); MS (ESI): $[M+H]^+$ found 259; requires 259.282. Anal. Calcd for $C_{11}H_{18}O_5N_2$: C, 51.15; H, 7.03; N, 10.85. Found: C, 40.42; H, 5.69; N, 8.08.

3.3.2. *N,N′*-Diallylxylardiamide (3a)

The starting material dimethylxylarate (**2a**) was prepared from D-(+)-xylose as described in Section 3.3.1. Compound **2a** (15.0 g, 71.9 mmol) was dissolved under argon in dry tetrahydrofuran (150 mL) in 250 mL glass flask. Allylamine (16.2 mL, 215.6 mmol) was added and the temperature was raised to 70 °C. After 24 h the solution was cooled and the crystals were filtered and washed with THF/10% ethanol-solution (80 mL). Light yellow crystals were recrystallized from ethanol, yield 7.0 g (37%): mp 181–185 °C (lit.: 166–170 °C).[17] IR: ν 3417 (amide I), 3080 (CH=), 1638 (CO), 1546 (amide II), 1125 (OH) cm^{-1}. ^{1}H NMR (Me_2SO-d_6, 300 MHz): δ 7.83 (t, 2H, NH, J = 5.9 Hz, J = 11.9), 5.84 (m, 2H, allyl =CH, J = 1.8 Hz), 5.50 (d, 2H, OH-2/4, J = 5.7 Hz), 5.13 (m, 4H, allyl CH_2=, J = 1.8 Hz), 4.81 (d, 1H, OH-3, J = 7.3 Hz), 4.11 (dd, 2H, H-2/4, J = 5.7 Hz, J = 4.1 Hz), 3.95 (m, 1H, H-3, J = 7.3 Hz, J = 4.1 Hz),

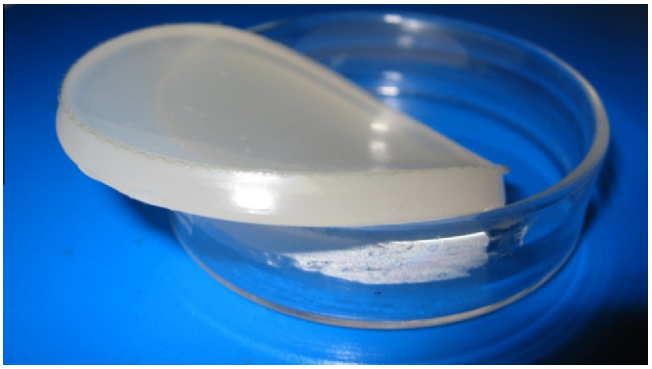


Figure 5. Hydrogel prepared from HPX-A with 5 wt % of DAA cross-linker.

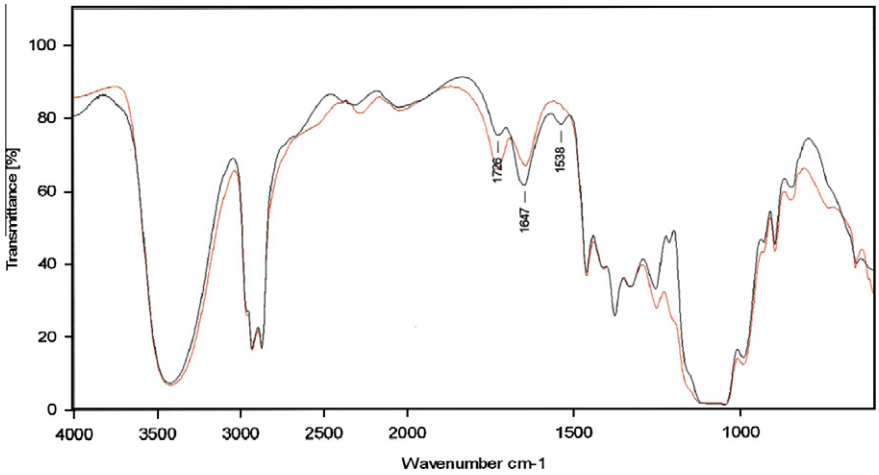


Figure 6. IR spectrum of HPX-BA (red spectrum) and the spectrum of HPX-BA cross-linked with 5 wt % of DAT (black spectrum).

Table 1
The incorporation efficiency (*E*) of DA cross-linkers calculated from elemental analysis of hydrogels cross-linked with 5 wt % of cross-linker

	HPX-A (wt %)	*E* (%)	HPX-BA (wt %)	*E* (%)	X-BA (wt %)	*E* (%)
DAT	3.86	77	3.79	76	2.07	41
DAG	3.72	74	3.34	67	1.67	33
DAA	3.53	71	2.96	59	1.56	31
DAX	2.63	53	2.22	44	1.48	30

Table 2
Crosslinking efficiency of allylic double bonds calculated from the amounts of bromine found with instrumental neutron activation method

Sample	Br-content (wt %)	DS_A (Br)	DS_A (^{1}H NMR)	DS_B (^{1}H NMR)	DS_{HP} (^{1}H NMR)
Xylan	0.04	0	0	0	
HPX-A	13.7	0.20	0.36	0	0.85
HPX-A cross-linked	11.3				
HPX-BA	6.5	0.10	0.17	0.34	0.63
HPX-BA cross-linked	4.4				
X-BA	10.9	0.20	0.38	0.75	0
X-BA cross-linked	5.4				

Degrees of substitution determined by the bromination and ^{1}H NMR methods are also presented.

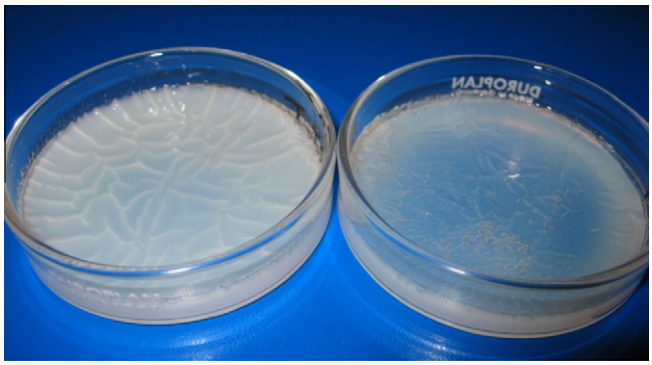


Figure 7. The opaqueness of HPX-BA hydrogels with 5 wt % (left) and 1 wt % (right) of DA cross-linker.

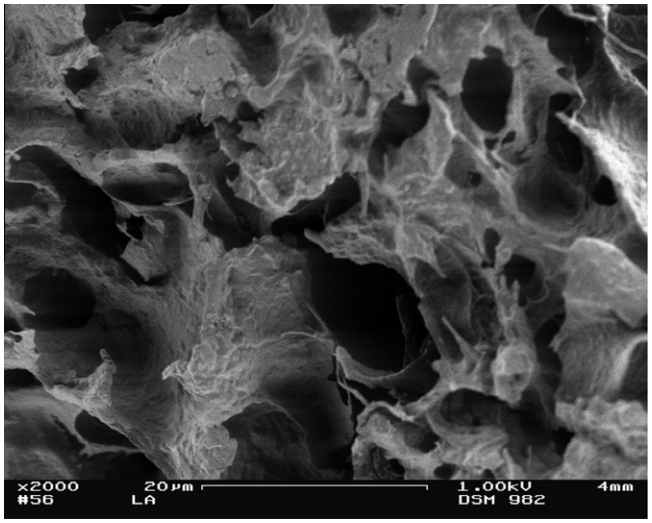


Figure 8. SEM images of X-BA hydrogel without DA cross-linker. The scale is 20 µm.

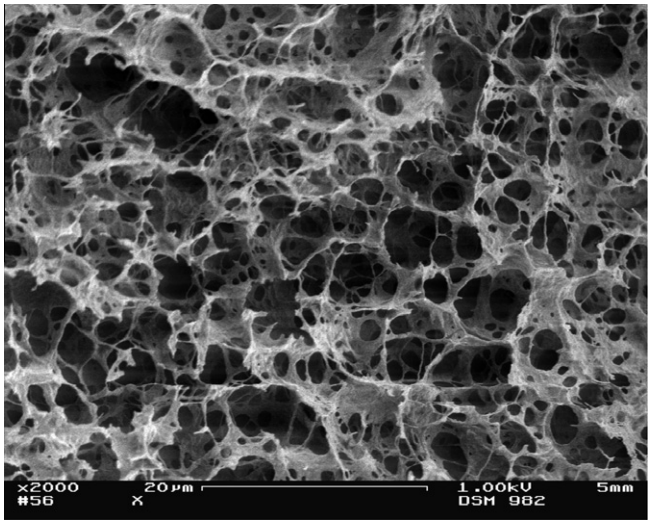


Figure 9. SEM image of X-BA hydrogel with 1 wt % of DAX cross-linker. The scale is 20 µm.

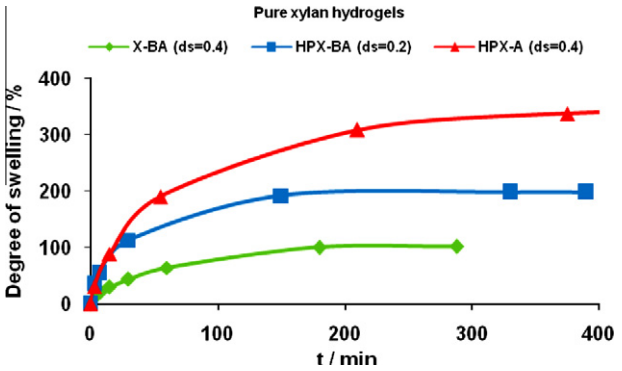


Figure 10. Swelling curves of X-BA, HPX-BA, and HPX-A without DA cross-linkers.

3.76 (m, 4H, $-CH_2-$NH, J = 5.9 Hz); ^{13}C NMR (Me_2SO-d_6, 75 MHz): 173.3 (CONH), 136.2 ($-CH{=}CH_2$), 115.9 ($-CH{=}CH_2$), 73.5 (C-2 ja C-4), 72.9 (C3), 41.6 (CH_2-NH); MS (ESI): $[M+H]^+$ found 259; requires 259.282. Anal. Calcd for $C_{11}H_{18}O_5N_2$: C, 51.15; H, 7.03; N, 10.85. Found: C, 46.28; H, 6.38; N, 9.52.

3.3.3. *N,N′*-Diallylgalactardiamide (3c)

Galactaric acid (**1c**) was esterified with methanol according to Kiely et al.[22] Dimethylgalactarate (**2c**) (26.5 g, 111.3 mmol) was dispersed in dry tetrahydrofuran (400 mL) under argon in 1 L glass reactor. Allylamine (25.1 mL, 334 mmol) was added and the temperature was raised to 70 °C. After 48 h the solution was cooled and the crystals filtered and washed with THF/10% ethanol-solution (300 mL). Recrystallization from water gave pure white crystals, yield 19.1 g (59%): mp 215–220 °C (lit. 207–210 °C);[17] IR: ν 3290 (amide I), 3084 (CH=), 1634 (CO), 1537 (amide II), 1047 (OH) cm^{-1}. ^{1}H NMR (Me_2SO-d_6, 300 MHz): δ 7.73 (t, 2H, –NH, J = 12.1 Hz, J = 6.0 Hz), 5.84 (m, 2H, allyl =CH, J = 5.1 Hz, J = 10.2 Hz,) 5.28 (d, 2H, OH-2/5, J = 7.1 Hz), 5.14 (m, 4H, allyl CH_2=, J = 5.1, J = 10.3), 4.45 (dd, 2H, OH-3/4, J = 2.5, J = 8.6), 4.2 (d, 2H, C-2/5, J = 7.1), 3.84 (dd, 2H, C-3/4, J = 2.1, J = 8.6), 3.78 (t, 4H, $-CH_2-$NH, J = 5.5, J = 11.0 Hz); ^{13}C NMR (Me_2SO-d_6, 75 MHz): 174.2 (CONH), 136.3 ($-CH{=}CH_2$), 115.8 ($-CH{=}CH_2$), 71.7 (C-2/3/4/5), 41.6 (CH_2 –NH); MS (ESI): $[M+H]^+$ found 289; requires 289.308. Anal. Calcd for $C_{12}H_{20}O_6N_2$: C, 49.99; H, 6.99; N, 9.72. Found: C, 49.85; H, 6.93; N, 9.71.

3.4. Xylan derivatization

3.4.1. Hydroxypropylated xylan

Never-dried (7.5 wt % of xylan, containing 0.9% NaOH) or dried xylans extracted, for example, from (bleached) birch pulp were used as starting materials. The pH and/or sodium hydroxide content was adjusted to pH 11–13 and/or 0.5–2.0 M. The mixture was first stirred for 1 h at 65 °C and then cooled down to room temperature. Propylene oxide was added into the reaction mixture keeping temperature at 15 °C. After the addition of propylene oxide the reaction mixture was let to warm up slowly to room temperature and to react for 24 h. After the reaction the pH was adjusted to 6–7 with ~6 M HCl. Xylan derivatives were first precipitated using acetone (five times volume compared to the amount of water in the reaction mixture) and purified by dialysis for two nights, first night in running tap water and the second night in standing deionized water (suitable membrane cut-off was 3500 Da), concentrated, and finally freeze-dried.

3.4.2. Derivatization of hydroxypropylated xylan with butyl and allyl glycidyl ether

600 mL (627 g, 11.4 wt % of xylan) of hydroxypropylated xylan solution was placed in a 1-l reactor with a mechanical stirrer.

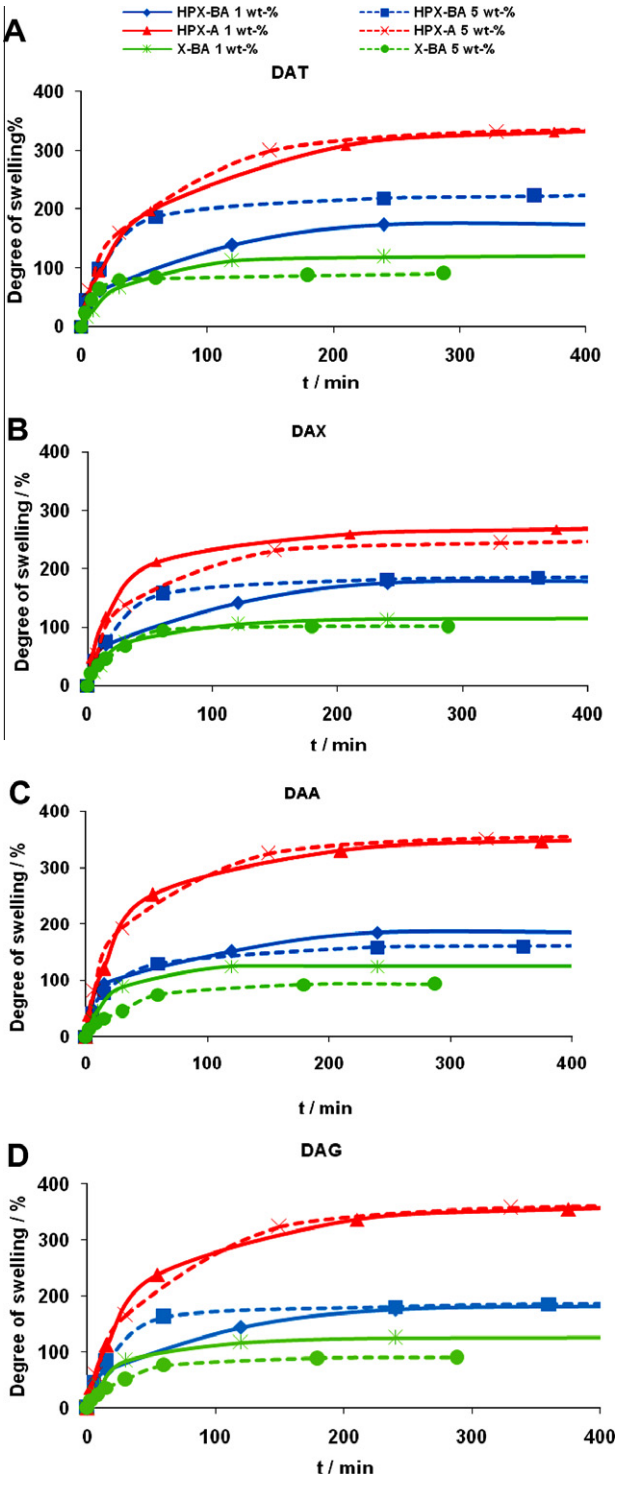


Figure 11. Swelling curves of HPX-BA, HPX-A, and X-BA cross-linked with (A) DAT, (B) DAX, (C) DAA, and (D) DAG. The solid line represents cross-linking with 1 wt % and the dashed line cross-linking with 5 wt % of DA.

The sodium hydroxide content of the solution was adjusted to 1.0 M. The mixture was first stirred for 1 h at 65 °C and then 24 h at room temperature. The solution was heated to 45 °C under argon. Butyl glycidyl ether (64.5 mL) and allyl glycidyl ether (28.7 mL) were mixed and added dropwise into the reaction mixture and left to react for 24 h at 45 °C. The solution turned white and turbid. After cooling the reaction mixture turned into a brownish solution and the pH was adjusted to 6–7 with ~6 M HCl. The

product was first precipitated with 4 L of acetone, left to settle overnight and washed with 2 × 1 L of acetone. Excess acetone was decanted and the precipitate left to dry in air overnight. The product was dissolved in 250 mL of water and purified by dialysis for two nights, first night in running tap water and the second night in standing deionized water (suitable membrane cut-off was 3500 Da) and finally freeze-dried to obtain 26.9 g of white crystalline solid. More product was obtained by evaporating the acetone from the supernatant remaining from the precipitation step. A slimy residue was obtained after pouring out the excess water. The residue was diluted with a small amount of ethanol, and dialyzed and freeze-dried as previously described to obtain 32.9 g of pure product. Overall yield 59.8 g (38%).

3.4.3. Derivatization of hydroxypropylated xylan with allyl glycidyl ether

The reaction was performed as in Section 3.4.2 but *t*-BuOH (364 mL) was added as a co-solvent to the reaction mixture and only allyl glycidyl ether (77 mL) was used. The entire product was obtained from the precipitation step. Yield was 47.4 g (41%).

3.4.4. Derivatization of xylan with allyl and butyl glycidyl ethers

700 mL (750 g, 7.3 wt % of xylan) of a suspension containing 51.1 g of the non-dried xylan was used as a starting material. NaOH concentration of the suspension was 0.8 M. The reaction mixture was first heated to 65 °C for 2 h. 100 mL of butyl glycidyl ether was slowly added (50 min) and let to react overnight. 50 mL of allyl glycidyl ether was slowly added (50 min) and let to react for an additional 24 h. The reaction mixture was adjusted to pH 7–8 with 37% HCl. The neutralized reaction mixture was slowly poured into 2.5 L of acetone, excess acetone was decanted, and the precipitate left to dry in air overnight. The product was purified by dialysis. The dialyzed xylan in water was freeze-dried yielding 76 g (40%) of solid white powder.

3.5. Preparation of hydrogels

To a solution of 2.0 g of xylan derivative with or without 1 or 5 wt % of DA cross-linker in 20 mL of deionized water, 100 mg (5 wt %) of radical initiator potassium persulfate was added. The solution was poured onto a Petri dish, placed in an UV oven and polymerized under UV light for 3–4 min during which the gels turned more white and turbid. After cross-linking the gels were washed several times with deionized water to remove any unreacted material and salts. The gels were dried in a vacuum oven in 40 °C for 48 h or by freeze-drying. Before freeze-drying the wet gels were immersed in liquid nitrogen.

3.6. Bromination

The samples (2 g) were stirred in chloroform (68 mL) for 18 h protected from light. All the samples were insoluble to chloroform. A 12% solution of bromine in chloroform was freshly prepared and 10 mL was added to each reaction mixture until a slight excess of bromine remained. The samples were stirred for 2 h and subsequently washed with methanol, aqueous sodium thiosulfate (10%, w/v), water and once again with methanol. The samples were dried in a vacuum oven in 40 °C for 24 h.

3.7. Swelling assessments

For swelling measurements, the gel samples were dried to a constant weight in 40 °C in a vacuum oven (m_{dry}) and immersed in excess of deionised water at room temperature. Excess water was removed with a dry filter paper and the sample (m_{wet}) weighed at time intervals. The gels were evaluated in triplets and the mean degree of swelling was then calculated. The degree of swelling was determined by the following equation:

$$\text{Degree of swelling} = \frac{m_{wet} - m_{dry}}{m_{dry}} * 100\%$$

4. Conclusions

Novel hydrogels were synthesized using bio-based starting materials. Xylan was derivatized to different degrees of substitution of 1-allyloxy-2-hydroxy-propyl (A) groups combined with 1-butyloxy-2-hydroxy-propyl (B) and/or hydroxypropyl (HP) groups. The sugar diacids used as cross-linkers were derivatized chemically to *N,N′*-diallylaldardiamides (DA). The most important correlation was observed between the cross-linking efficiency of the allylic double bonds and the water absorbency. The water absorbency (up to 350%) was highest for hydrogels prepared from HPX-A with the lowest cross-linking efficiency 18%. Contrarily, the lowest water absorbency (about 100%) was observed for hydrogels prepared from X-BA with the highest cross-linking efficiency of 50%. When the cross-linking efficiency of allylic double bonds of xylan derivatives increases the incorporation of an additional DA cross-linker into the hydrogel network decreases. However, the amount of DA cross-linkers had only a small influence on the water absorbencies. The use of DA cross-linkers in the preparation of hydrogels had an influence on the pore structure making it more uniform. The effect of HP and B substituents to water absorbency was not so clear: the HP groups in the xylan backbone of HPX-A (DS_{HP} 0.9) and HPX-BA (DS_{HP} 0.6) seemed to increase the water absorbency probably due to longer side chains enabling a more open structure. The more hydrophobic B groups in HPX-BA (DS_B 0.3) and X-BA (DS_B 0.8) hydrogels may also have a negative effect on the water absorption properties.

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