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Amide-linked *N*-methacryloyl sucrose containing polymers

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ABSTRACT

1′,2,3,3′,4,4′,6-Hepta-*O*-benzyl-6′-*N*-methacryloyl-6′-deoxysucrose **1**, 6′-deoxy-6′-*N*-methacryloyloxyethylureido sucrose **2** and 6,6′-dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose **3** have been homo-polymerized and copolymerized with styrene by a free radical process, yielding polymer materials with pendant sucrose moieties, attached to the polymer backbone via amide linkages. The results demonstrated that varying the structural features of the monomers, greatly affected the thermal and rheological properties of the polymers. The polymer materials obtained have been characterized by NMR, MALDI-TOF, DSC, AFM and EWC (equilibrium water content). The efficient synthesis of the three novel, regioisomerically pure, *N*-methacryloylamide sucrose-containing monomers (**1**, **2** and **3**) have been described.

1. Introduction

Amphiphilic and hydrogel polymers are useful biomedical materials. Self-assembly of amphiphilic polymers is a typical example of advanced functional polymers. There have been reported numerous examples of preparing nanoparticles from water-soluble amphiphilic polymers as functional materials possessing potential applications, including drug delivery, enzyme encapsulation and nanoparticle catalysis (Caruso, Trau, Mohwald, & Renneberg, 2000; Gaponik et al., 2003; Lu et al., 2001). If natural resources, such as saccharides, are used for production of polymers, their applicability would expand furthermore (Akiyoshi, Deguchi, Moriguchi, Yamaguchi, & Sunamoto, 1993; Breslow & Zhang, 1996). The choice of natural compounds as starting materials is based on the understanding that to minimize risks in designing new self-assembling molecules, one must try to imitate and modify natural designs to ensure biocompatibility.

It is known that a very important advantage of naturally derived polymers as drug delivery systems over synthetic analogs is their innate biocompatibility and biodegradability. However, to extract proteins and polysaccharides from animals is often expensive and with batch-to-batch variations. Due to the complexity of these structures, it is difficult to introduce fine structural modification to promote other specific functions in order to obtain properties necessary for other potential applications. The design of polymers and oligomers that mimic the complex structures and remarkable biological properties of proteins is an important task with both fundamental and practical implications (Liao, Yu, & Guan, 2009; Tew et al., 2002).

It is in this sense that we aim to combine the advantages from natural compounds and synthetic systems, namely, the biocompatibility and biodegradability of natural components and to explore the potential structural versatility obtainable through synthetic chemistry. Our group has been exploring strategies to design synthetically simple, highly functional, and biocompatible novel biomaterials from natural building blocks (Barros & Petrova, 2009; Barros, Petrova, & Ramos, 2004, 2007).

Another feature that is expected to enhance the biocompatibility and bio-recognition is the presence of amide linkage, which mimics the repeating structural unit of proteins. N-methacryloyl polymers have found various applications as stimuli-responsive polymers (Luo, Zhao, & Li, 2012) affinity chromatography and protein recognition (Corman & Akgol, 2012), drug-delivery systems (Chang, Chen, Zhong, Chang, & Liang, 2012), etc. We aimed to combine this functionality with pending sugar moieties, which have been shown to bestow hydrophilic, biocompatible and biodegradable properties (Barros, Petrova, & Singh, 2010a; Varma, Kennedy, & Galgali, 2004). Particularly, sucrose is a carbohydrate feedstock of low molecular weight which is ubiquitous in its availability and is of relatively low cost. Since sucrose has eight chemically active hydroxyl groups, we have developed its regioselective derivatization for the selective synthesis of sucrose-containing linear polymers (Barros,

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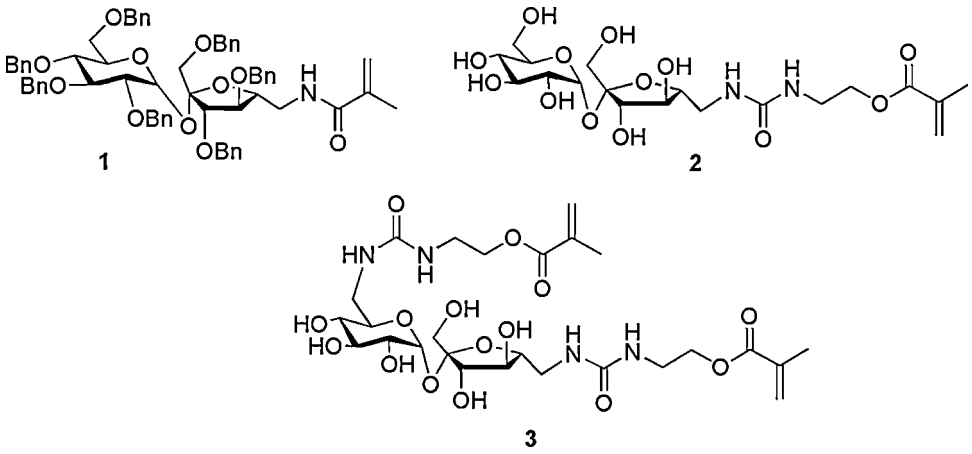


Fig. 1. Structures of N-methacryloyl sucrose monomers **1**–**3**.

Petrova, & Correia-da-Silva, 2011; Barros, Petrova, Correia-da-Silva, & Potewar, 2011).

The introduction of functional groups (mesogenic, chromophoric, etc.) into side-chains of poly-methacrylates leads to principally new materials which can be considered as binary systems, consisting of a polymer matrix with distributed functional groups. The latter are anchored by only one end to the polymer backbone, providing a relative independence in the motion of the backbone and side-chains. As a result, comb-like polymers with side-chain functional groups combine functional and polymeric properties. Such systems are used as working elements in nonlinear optics, holography, information storage and recording devices (Moscicki, 1992; Yesodha, Pillai, & Tsutsumi, 2004).

In our case, each structural unit of the polymer is an amphiphile consisting of hydrophilic carbohydrate and hydrophobic vinylbenzyl (styryl) moieties. It has been shown that monosaccharide-containing polystyrenes have a strong affinity for organic solutes in water. The binding ability was assumed to be attributable to the tightly coiled conformation induced by their amphiphilic structures (Kobayashi, Sumitomo, & Ina, 1985).

Herein, the synthesis of three novel *N*-methacryloyl sucrose monomers with different structural characteristics is reported (Fig. 1). Monomer **1,** which contains one polymerizable double bond and sucrose with protected hydroxyl groups with benzyl ether moieties, is expected to form hydrophobic linear polymers, easily soluble in a variety of organic solvents. Monomer **2,** also with one polymerizable double bond, but with free hydroxyl groups, yields linear hydrophilic and swellable in water polymers, soluble in polar solvents; while monomer **3**, which features two double bonds and free hydroxyl groups, produces hydrophilic cross-linked hydrogel also swellable in water, but insoluble in any solvent. Several procedures for free-radical homopolymerization of monomers **1**–**3** and copolymerization with styrene were described, which produced linear hydrophobic and hydrophilic polymers and cross-linked hydrogels. The experimental results demonstrated how varying the structural features of the monomers involved, greatly affected the thermal, mechanical and rheological properties of the polymers. The resulted polymer materials were characterized by NMR, MALDI-TOF, DSC and AFM. Their ability to swell and absorb water has been studied as well.

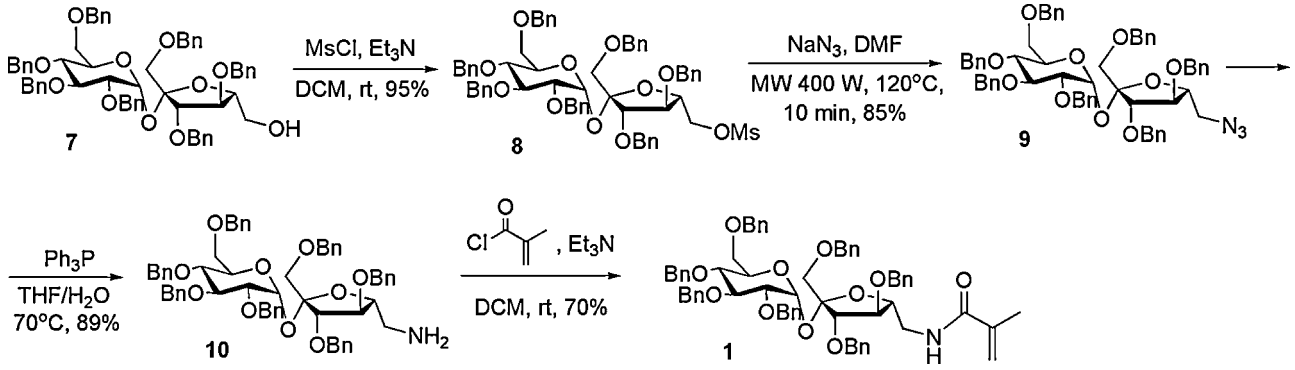
2. Results and discussion

2.1. Synthesis of monomers

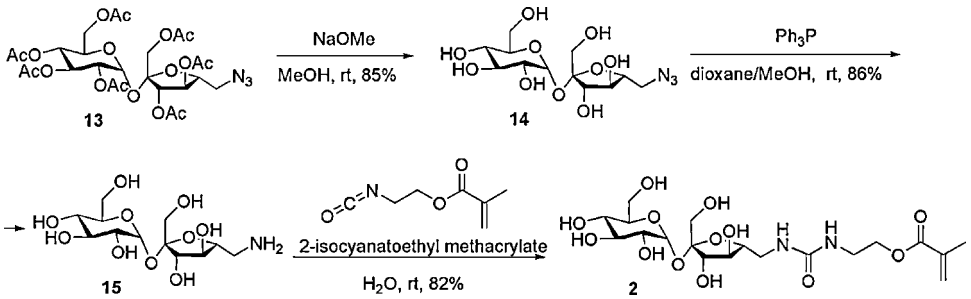
2.1.1. Synthesis of 1′,2,3,3′,4,4′,6-hepta-O-benzyl-6′-N-methacryloyl-6′-deoxysucrose **1**

In order to obtain 6′-amino-6′-deoxysucrose **10**, a synthetic strategy through the intermediate 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-sucrose **7** (Barros et al., 2004) was used (see Supplementary Data).

Compound **7** was treated with methanesulfonyl chloride in DCM in the presence of Et_3N and DMAP at 0 °C (Scheme 1). By using 1.1 equivalent of methanesulfonyl chloride, the reaction afforded 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-*O*-mesyl-sucrose **8** in excellent yield (95%). Next, compound **8** was treated with NaN_3 in DMF under microwave irradiation at 400 W, 120 °C for 10 min, to afford 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-azido-6′-deoxysucrose **9** in 85% yield. To reduce the azide group to amine, the azide **9** was treated with Ph_3P in THF/H_2O at room temperature, but it did not react. Then the reaction was carried out at elevated temperature and



Scheme 1. Synthesis of monomer **1**.



Scheme 2. Synthesis of monomer **2**.

it proceeded smoothly at 70 °C to afford 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-amino-6′-deoxysucrose **10** in excellent yield (89%). Next, the amine **10** was treated with methacryloyl chloride in DCM in the presence of Et_3N and catalytic amount of DMAP at 0 °C, followed by stirring at room temperature. Thus, the desired monomer **1** was obtained in 70% yield (Scheme 1). All the compounds were characterized by IR, ^1H NMR, ^{13}C NMR spectroscopic and mass analysis. The ^1H NMR spectrum of compound **1** (see Supplementary Data) showed the characteristic peaks: doublet at δ 5.62 ppm, singlet at δ 5.59 ppm and singlet at δ 1.88 ppm. The ^{13}C NMR spectrum of compound **1** showed characteristic peaks at δ 168.38 (*C*O), 139.8 (CO—*C*=CH_2), 119.5 (C—CH_2), 42.5 (CH_2—NH—), 18.5 (CH_3) ppm. Thus, we have achieved the synthesis of monomer **1** from sucrose **4** in overall yield of 29% in 7 steps.

2.1.2. Synthesis of 6′-deoxy-6′-*N*-methacryloyloxyethylureido sucrose **2**

In continuation of our interest on new polymerizable sucrose monomers, herein we present the regioselective synthesis of a new hydrophilic sucrose monomer **2**, 6′-deoxy-6′-*N*-methacryloyloxy ethylureido-sucrose, in which the polymerizable double bond is pendent from the sucrose core with a linker. It was designed with a spacer in order to distance the acrylic group from the rigid sucrose moiety, giving more flexibility and less steric hindrance for subsequent polymerization steps, as suggested in the literature (Anders et al., 2006).

The compound 1′,2,3,3′,4′,4,6-hepta-*O*-acetyl-6′-azido-6′-deoxy-sucrose **13** was obtained as previously described (see Supplementary Data) (Potewar, Petrova, & Barros, 2013). The next step was deprotection of the acetyl groups, for which the azide **13** was treated with sodium methoxide in dry MeOH at room temperature to afford 6′-azido-6′-deoxy-sucrose **14** in 85% as colorless solid (Scheme 2). The spectroscopic data of this compound matches the reported in literature (Singh, Maynard, Doyle, & Taylor, 1984). When the azide **14** was treated with Ph_3P in dioxane/MeOH at room temperature, it afforded the desired 6′-amino-6′-deoxy-sucrose **15** (Sharma, Norula, & Mattey, 1982; Singh et al., 1984) in 86% as faint pale yellow solid. Then **15** was treated with 2-isocyanatoethyl methacrylate in H_2O at room temperature to afford the monomer **2**, 6′-deoxy-6′-*N*-methacryloyloxyethylureido sucrose, as colorless solid in 82% yield (see Supplementary Data).

2.1.3. Synthesis of 6,6′-dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose **3**

The compound 6,6′-diamino-6,6′-dideoxysucrose **18** has been obtained as previously described (Barros, Petrova, Correia-da-Silva, et al., 2011) via 6,6′-dibromo-6,6′-dideoxysucrose **16** and 6,6′-diazido-6,6′-dideoxysucrose **17** (see Supplementary Data).

Then, by a similar procedure as described above, the diamine **18** was reacted with 2 equiv. of 2-isocyanatoethyl methacrylate in H_2O at room temperature to afford the monomer **3**, 6,6′-dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose (Scheme 3), as colorless solid in 63% yield (see Supplementary Data).

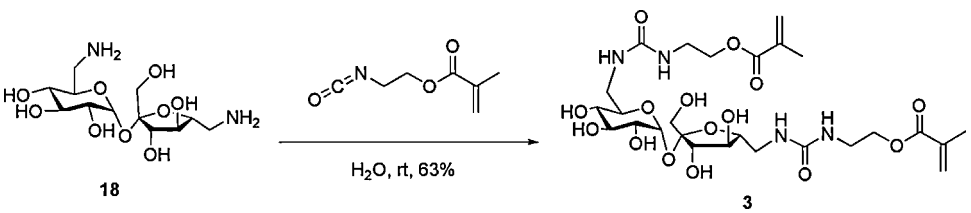
2.2. Synthesis and characterization of polymers

2.2.1. Polymerization methods

Using the novel sucrose monomers **1**–**3**, several different types of polymers have been synthesized by free radical homo- and co-polymerization (See ESI, Schemes S7–S9 and Table 1). The polymerization conditions, reaction time, and the initial monomers ratio have been optimized as previously described (Barros et al., 2004; Barros & Petrova, 2009; Barros et al., 2007; Barros, Petrova, & Singh, 2010a, 2010b).

As a result we obtained a number of copolymers with diverse contents of pending sucrose moieties (estimated by ^1H NMR), with different chain length, reported by the mass average molecular weight, M_w, number average molecular mass, M_n, and polydispersity, M_w/M_n (measured by MALDI-TOF), and with different physical properties such as glass transition temperatures, Tg (measured by DSC), ability to swell and absorb water, and the surface morphology of thin films, which has been examined by AFM (Atomic Force Microscopy).

For the homo-polymerization of monomer **1** and its co-polymerization with styrene (10 mol equiv.) have been used homogeneous solution polymerization (see ESI, Scheme S7). It has been examined in the presence of AIBN as free-radical initiator in toluene at 70 °C, followed by precipitation in cold ethanol (which was miscible with the monomers, the solvent, and by-products, such as oligomers), to produce solid polymers poly(*N*-(methacrylamido)-1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-amino-6′-deoxysucrose) **19** and poly(*N*-(methacrylamido)-1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-amino-6′-deoxysucrose)-co-polystyrene **20**. The sugar content in



Scheme 3. Synthesis of monomer **3**.

Table 1
Free radical homo- and co-polymerization with styrene of sucrose monomers **1**–**3**.

Polymer	Monomers	Polymerization procedure; Yield of solid polymer	$\frac{[sug]_0^a}{[styr]_0}$	$\frac{[sug]^b}{[styr]}$	M_n[c] [g/mol]	M_W[c] [g/mol]	M_w/M_n	Tg[d] [°C]	Swelling in H_2O [%]
19	**1** (homo-polymer)	Toluene/AIBN 70 °C, 24 h 14%	–	–	3230	3740	1.16	69	Hydrophobic
20	**1** + styrene	Toluene/AIBN 70 °C, 24 h 48%	0.1	0.03	3780	4010	1.06	72	Hydrophobic
21	**2** (homo-polymer)	$H_2O/Na_2S_2O_8$ 70 °C, 24 h 18%	–	–	3280	3540	1.08	−27	250
22	**2** + styrene	DMF/AIBN 70 °C, 24 h 14%	0.1	0.44	4710	5320	1.13	64	160
23	**3** (homo-polymeric hydrogel)	$H_2O/Na_2S_2O_8$ 70 °C, 24 h 20%	-	–	Not measured – insoluble sample				
24	**3** + styrene (dispersion copolymerization)	H_2O + toluene/$Na_2S_2O_8$ 70 °C, 24 h 53%	0.1	0.09	Not measured – insoluble sample				

[a] Initial (feed) mol ratio of the monomers. [b] Mole ratio of the co-monomers in the copolymer, determined by ^{1}H NMR. [c] Determined by MALDI-TOF. [d] Determined by DSC.

the obtaining polymer **20** was 3 mol%. Both polymers were easily soluble in a variety of organic solvents such as toluene, xylene, benzene, hexane, dichloromethane, chloroform, etc.

Poly(6,6′-dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose) **21** was obtained by precipitation polymerization (See ESI, Scheme S8). Monomer **2** was dissolved in oxygen-free H_2O under argon atmosphere with sodium persulfate $Na_2S_2O_8$ (1%) as radical initiator, and heated at 70 °C for 24 h. The polymer was separated from the resulting heterogeneous reaction mixture by filtration, washed with cold methanol, and dried under vacuum. The polymer **21** was obtained in 18% yield and was characterized as amorphous solid.

The co-polymerization of monomer **2** with styrene has been examined in the presence of AIBN as free-radical initiator and in DMF as solvent, at 70 °C under an Ar atmosphere, followed by precipitation in cold acetone to yield polymer **22** poly(6,6′-dideoxy-6,6′-*N*-dimethacryloyloxy ethylureido sucrose)-co-polystyrene with 44 mol% sugar content and 14% yield of solid polymer in respect to the initial monomer mixture. DMF was chosen as media for the co-polymerization because it dissolves well both monomers – the hydrophilic sugar monomer **2**, as well the hydrophobic styrene (homogeneous solution polymerization). In these conditions was observed lower conversion of styrene, but higher incorporation of the sugar monomer unit. The filtration and washing of the precipitate with acetone, and repeated dissolution and re-precipitation, assured the removal of unreacted monomers, as they were soluble in acetone. The polymers **21** and **22** were soluble in polar organic solvents, as DMF and DMSO.

Homo-polymeric hydrogel poly(6,6′-dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose) **23** (See ESI, Scheme S9) was prepared from monomer **3** by a similar technique used for **21** by free-radical precipitation polymerization initiated by sodium persulfate $Na_2S_2O_8$ (1%) in oxygen-free H_2O as solvent. The resulted heterogeneous reaction mixture was filtered and washed thoroughly with H_2O and then cold methanol to remove any residual monomer, to yield insoluble powder of cross-linked hydrogel **23** (yield 20% from the monomer weight).

For the co-polymerization of **3** with styrene, dispersion polymerization (Jung, Huh, Cheon, & Park, 2009) was performed to yield the hydrogel **24,** poly(6,6′-dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose)-co-polystyrene. For this, two solutions were prepared: water solution, containing the hydrophilic sugar monomer and the radical initiator sodium persulfate $Na_2S_2O_8$ (1%); and toluene solution of styrene. Oil-in-water emulsion was formed by combining the two solutions and dispersing them by vigorous stirring. Then the emulsion was heated at 70 °C for 24 h while stirred vigorously. After cooling, the resulted heterogeneous mixture was treated as described above, to yield the cross-linked hydrogel **24** as insoluble white powder in 53% yield in respect to the initial monomer mixture.

In the last two procedures the bis-methacryloyl sucrose derivative **3** acted as cross-linker. Estimation of degree of cross-linking was attempted by two different methods (Glavchev, Petrova, & Devedjiev, 2002a, 2002b) – by IR spectrometry and the amount of gel fraction after extraction in a Soxhlet extractor. The IR spectra of the solid polymer samples **23** and **24** did not show any signals corresponding to the vinyl groups of the monomers, which led to conclusion that any unreacted monomers have been removed during the work-up.

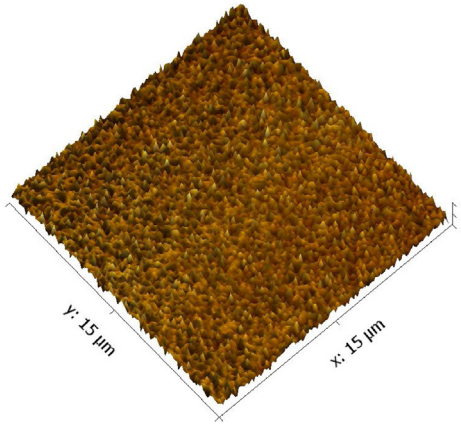
The degree of cross-linking by the amount of gel fraction can be found as a ratio between the sample mass after extraction and the initial sample mass, in percentages. In our case, four hours extraction in a Soxhlet extractor did not yield any soluble fractions for the two samples, which corresponds to degree of cross-linking 100%. Therefore, to further characterize the polymer **24**, the residue of unreacted monomers mixture, after isolating the solid polymer **24**, have been analyzed. By ^{1}H NMR it was estimated to contain 11 mol% of sugar monomer **3**, and 89 mol% styrene. From this data, knowing that the monomers feed ratio was sugar/styrene 1:10 and that the yield of solid polymer was 53%, the monomers units contained in the obtained polymer **24** have been calculated to be 8 mol% sugar and 92 mol% styrene, or sugar/styrene ratio 0.09. Assuming that the sugar and styrene units were randomly distributed in the polymer chains, the length of the linear polymer segments was estimated to be on the average around six styrene units.

2.2.2. ^{1}H NMR

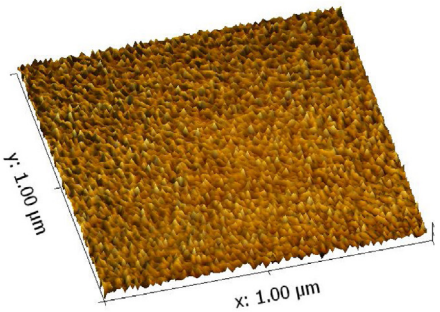
The copolymer compositions were determined by ^{1}H NMR by comparing the peak areas of the aromatic protons present in the styrene unit with the 14 sucrose unit protons. In co-polymer **22** a higher incorporation of sugar (0.44 molar parts) than in the co-polymer **20** (0.03 molar parts) by approximately one order of magnitude was achieved. This result was expected based on the structures of the monomers **1** and **2** – in monomer **2** the polymerizable double bond is positioned farther from the rigid sucrose skeleton, thus providing more flexibility and facilitating its participation in the co-polymerization. Even more, in monomer **1** the hydroxyl groups of sucrose are protected with benzyl groups, which make it bulkier and increase the steric hindrance. The value for co-polymer **20** is in agreement with data previously obtained for monomers with similar structural features, (Barros et al., 2004, 2010a) while the incorporation of sugar moieties in co-polymer **22** was found to be significantly improved.

2.2.3. MALDI-TOF

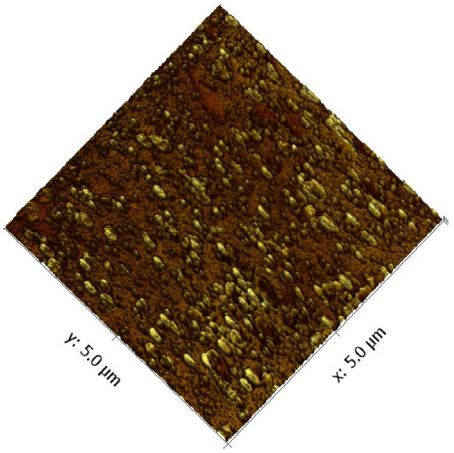
MALDI-TOF measures the mass very accurately, and it gives an absolute measurement of mass. Still, the choice of the most suitable matrix for the sample and solution conditions have to be optimized for unconventional polymers, as is the case of



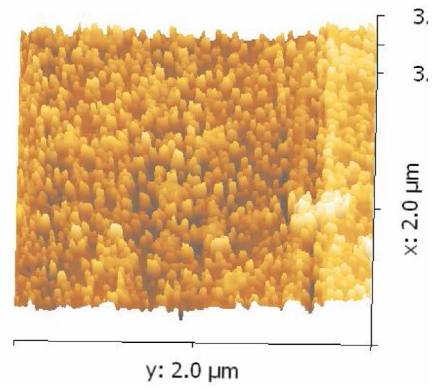
2.1. Polymer **19**, 15 µm.



2.2. Polymer **20**, 1 µm.



2.3. Polymer **21**, 5 µm.



2.4. Polymer **22**, 2 µm.

Fig. 2. AFM images of polymer films **19**–**22**.

poly(vinylsacharides). The results obtained are summarized in Table 1 (see SI for representative images).

The molecular weights of the co-polymers with styrene were higher than the weights of the respective homo-polymers. This difference could be due to steric reasons – the styrene units are smaller and act as spacers between bulkier sugar units; or chemical reactivity reasons – the larger amount of the sugar co-monomer, which is less reactive and also provides more possibilities for chain transfer reactions in the reaction mixture, leads to slower reaction and shorter chains. All the values of polydispersity obtained are very low, varying between 1.06 and 1.16, which means that the copolymers are very homogeneous.

2.2.4. *Differential scanning calorimetry (DSC)*

DSC main application is in studying phase transitions, such as melting, glass transitions, or exothermic decomposition. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity, thus providing information of the structure of the polymers. DSC traces of the six polymer samples can be seen in the SI, and the polymers glass transition temperatures (Tg) obtained from the DSC thermograms are presented in Table 1.

All the polymers synthesized were amorphous, bearing only glass transition temperature and neither crystallization nor melting temperatures were observed. The hydrophobic and styrene-containing polymers **19**, **20**, **22** and **24** exhibited similar Tg in the range 64–72 °C, while the homo-polymers consisting solely of hydrophilic sugar monomers, **21** and **23**, had much lower Tg (−20 and −27 °C, respectively). These results suggested that the presence of large amount of sucrose moieties in the polymeric matrix promoted a decrease in the polymer Tg, which indicated an increase of the polymer chains flexibility and malleability.

2.2.5. *Atomic force microscopy (AFM)*

The surface morphology and size distribution of the polymer samples were examined by AFM and representative images are shown in Fig. 2 and in ESI. The polymer films were obtained by suspending the polymer in a proper combination of good solvent/bad solvent (solvent shifting technique), followed by depositing the dilute dispersion onto freshly cleaved mica, then thorough drying. At these conditions, it was observed that the hydrophobic polymers **19** (Fig. 2.1.) and **20** (Fig. 2.2.) showed less ability for self-organization then the hydrophilic polymers **21** (Fig. 2.3.) and **22** (Fig. 2.4.). On the other side, the co-polymers with styrene **20** and **22** formed more uniform films then ones with high content of sucrose moieties **19** and **21**. The biggest and most uniformly shaped nanoparticles, with size ranging from 70 to 140 nm, were observed on the images of the hydrophilic polymer **21** film (Fig. 2.3).

2.2.6. *Equilibrium water content*

Equilibrium water content (EWC) of the hydrophilic polymer samples **21** and **22**, and the cross-linked hydrogels **23** and **24**, was

determined by immersing the samples in water at 25 °C for 24 h to complete equilibration. The excess surface-adhered liquid was removed by blotting and the swollen polymers were weighed using an electronic microbalance. Then the samples were dried in a vacuum oven at 40 °C for 10 h until constant weight. The EWC was calculated according to the following formula (Hou et al., 2006):

$$EWC(\%) = \frac{W_s - W_d}{W_d} \times 100\%$$

where W_s and W_d denote the weight of swollen and dried polymer samples, respectively.

The results obtained (Table 1) demonstrated the polymer's ability to swell and absorb water, which is important feature in many potential applications, as drug-delivery systems. The linear hydrophilic polymers **21** and **22** had higher EWC than the cross-linked hydrogels **23** and **24**, probably due to the restricted flexibility of the later because of the dense bonding network. Also, the styrene-containing polymers **22** and **24** absorbed less water than the homo-polymers **21** and **23**, due to the lower content of free hydroxyl groups. The polymer particles were translucent under swollen state, which is a typical feature of hydrogels. In general, the highest EWC showed polymer **21**, as high as 930%, which allowed us to classify it as superabsorbent polymer.

3. Conclusions

In summary, we have demonstrated the synthesis of different types *N*-methacryloylamide sucrose-containing monomers, regioisomerically pure and in good yields. These amides have been homo-polymerized and copolymerized with styrene by a free radical process, yielding polymer materials with pendant sucrose moieties. The polymer materials obtained have been characterized by NMR, MALDI-TOF, DSC, AFM and EWC (equilibrium water content), which showed that the structure of the resultant polymer was coincident with the theoretic structure. We are currently investigating a number of potential applications of these novel polymers including water-absorbent materials, biocompatible polymers and hydrogels, drug-delivery systems and solid supports for affinity chromatography.

4. Experimental

4.1. General

Reagents and solvents were purified by standard procedures (Perrin, Armagedo, & Perrin, 1980). NMR spectra were recorded at 400 MHz in $CDCl_3$ or D_2O, with chemical shift values (δ) in ppm downfield from TMS (0 ppm) or the solvent residual peak of D_2O (4.79 ppm) as internal standard. Optical rotations were measured at 20 °C on an AA-1000 polarimeter (0.5 dm cell) at 589 nm. The concentrations (c) are expressed in g/10^2 mL. Melting points were determined with a capillary apparatus with heating plate *Electrothermal* type, in open capillary on Buchi melting Point B-540 apparatus. FTIR spectra were recorded on Perkin-Elmer Spectrum BX apparatus in KBr dispersions or on NaCl cells. Mass Spectra were recorded on GC–TOF-MS (Gas Chromatography–Time Of Flight–Mass Spectrometer) Micromass, model GCT. The reactions under microwave irradiation were performed using a monomodal microwave reactor MicroSynth Labstation (MileStone, USA) (www.milestonesrl.com) in open flasks equipped with temperature control sensor and magnetic stirring. Differential scanning calorimetry (DSC) measurements were carried out on a Setaram DSC 131 scanning calorimeter equipped with a thermal analysis data system. Samples of 10 mg were placed in aluminum pans and sealed. The probes were heated two times, from −20 °C to 80 °C at a rate of 10 °C/min and from 25 °C to 250 °C under nitrogen atmosphere. MALDI-TOF spectra of polymers were recorded on Ultraflex III TOF/TOF Bruker equipped with laser type smartbeam and detecting system fast MCP-Gating. AFM images were acquired on a TT-AFM instrument from AFM Workshop in a vibrating mode.

N-(methacrylamido)-1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-amino-6′-deoxysucrose **1**:

To a solution of 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-amino-6′-deoxysucrose **10** (0.400 g, 0.41 mmol) in CH_2Cl_2 (6 mL) under inert atmosphere, was added Et_3N (68 μL, 0.493 mmol), followed by catalytic amount of 4-dimethylamino pyridine (DMAP). The reaction mixture was cooled to 0 °C in ice-water bath and methacryloyl chloride (44 μL, 0.452 mmol) was added. Then the reaction mixture was stirred for 20 min at 0 °C, followed by stirring at r.t. for 2 h. After completion of the reaction, reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude product, which was further purified by flash column chromatography (eluent, hexane/EtOAc; 3/1) to afford pure *N*-(methacrylamido)-1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-amino-6′-deoxysucrose **1** (70%, 0.300 g) as a viscous liquid.

$[\alpha]_D$ + 37.1 (c 1.0, $CHCl_3$).

IR (NaCl): ν_{max} 3403, 3066, 3006, 2920, 2855, 1668, 1518, 1496, 1457, 1366, 1215, 1081 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.27–7.11 (m, 35H, ArH), 6.43 (s, 1H, NH), 5.64 (s, 1H, —CO—C=C<u>H</u>), 5.61 (d, J = 2.4 Hz, 1H, H-1), 5.22 (s, 1H, —CO—C=C<u>H</u>), 4.90 (d, J = 11.0 Hz, 1H, Ph<u>CH$_2$</u>), 4.82–4.74 (m, 2H, Ph<u>CH$_2$</u>), 4.68–4.62 (m, 3H, 3H of Ph<u>CH$_2$</u>), 4.51–4.35 (m, 9H, 8H of Ph<u>CH$_2$</u>, H-5′), 4.08–3.94 (m, 4H, H-3′, H-4′, H-3, H-5), 3.78–3.40 (m, 8H, H-2, H-4, H-1′, H-6, H-6′), 1.89 (s, 3H, <u>CH$_3$</u>).

^{13}CNMR (100 MHz, $CDCl_3$): δ ppm 168.3 (CO amide), 139.8, 138.6, 138.3, 138.1, 138.0, 137.7 (Ar-<u>C$_{quat}$</u>), 128.3, 127.9, 127.7, 127.5 (Ar), 119.5 (—C=<u>CH$_2$</u>), 105.2 (C-2′), 90.7 (C-1), 83.8 (C-3′), 83.5, 81.7, 79.7, 77.6 (C-2, C-3, C-4, C-4′, C-5′), 75.4 (<u>CH$_2$</u>), 74.8 (<u>CH$_2$</u>), 73.3 (<u>CH$_2$</u>), 72.9 (<u>CH$_2$</u>), 72.8 (<u>CH$_2$</u>), 70.9 (C-5), 70.8 (C-6), 68.4 (C-1′), 42.6 (C-6′), 18.6 (<u>CH$_3$</u>).

MALDI TOF MS calcd for $C_{65}H_{69}NO_{11}Na$: $[M-H+Na]^+$ 1062.231; found 1062.414.

6′-Deoxy-6′-*N*-methacryloyloxyethylureido-sucrose **2**:

To a cooled solution of 6′-amino-6′-deoxy-sucrose **15** (0.280 g, 0.820 mmol) in H_2O (5 mL) at 0 °C, was added 2-isocyanato ethyl methacrylate (0.116 mL, 0.820 mmol) and the mixture was stirred at 0 °C for 2 h. The ice-water bath was removed; the reaction mixture was allowed to warm to r.t. and then stirred overnight. After completion of the reaction, reaction mixture was washed with CH_2Cl_2 (thrice) and was concentrated under reduced pressure to give crude oil which was purified by flash column chromatography (eluent; CH_2Cl_2/MeOH; 3/1) to afford 6′-deoxy-6′-*N*-methacryloyloxyethylureido-sucrose **2** (0.335 g, 82%) as colorless solid. m.p. 45–48 °C, dec. 150 °C to red color.

$[\alpha]_D$ + 41.8 (c 0.4, H_2O/CH_3OH 1:1).

IR (KBr): ν_{max} 3419, 2927, 1715, 1651, 1575, 1556, 1322, 1299, 1170, 1057 cm^{-1}.

^{1}H NMR (400 MHz, D_2O): δ ppm 6.04 (s, 1H, =C<u>H$_{2b}$</u>), 5.63 (s, 1H, =C<u>H$_{2a}$</u>), 5.28 (s, 1H, H-1), 4.07–4.14 (m, 2H, H-3′, H-6′), 3.94 (t, J = 8 Hz, 1H, H-4′), 3.65–3.74 (m, 5H, H-3, H-5, 2× H-6, H-6′), 3.56 (s, 2H, H-1′), 3.33–3.45 (m, 7H, H-2, H-4, H-5′, 2× C<u>H$_2$</u>), 1.83 (s, 3H, C<u>H$_3$</u>).

^{13}C NMR (100 MHz, D_2O): δ ppm 170.0 (CO ester), 160.0 (CO amide), 136.1 (—<u>C</u>(CH$_3$)=), 127.2 (=<u>CH$_2$</u>), 104.0 (C-2′), 92.4 (C-1), 80.2 (C-5′), 76.8 (C-3′), 76.0 (C-4′), 72.9 (C-3 and C-5), 71.4 (C-2), 69.8 (C-4), 64.7 (C-6′), 61.7 (C-1′), 60.8 (C-6), 43.1 (—<u>CH$_2$</u>), 39.0 (—<u>CH$_2$</u>), 17.7 (<u>CH$_3$</u>).

Anal. Calcd for $C_{19}H_{32}N_2O_{13}$: C, 45.97; H, 6.50; N, 5.64%. Found: C, 45.89; H, 6.55; N, 5.59%.

6,6′-Dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose **3**:

To a solution of 6,6′-diamino-6,6′-dideoxysucrose **18** (Barros, Petrova, Correia-da-Silva, et al., 2011) (0.5 g, 1.47 mmol) in water (6.5 mL) at 0 °C, was added 2-isocyanatoethyl methacrylate (0.413 mL, 2.93 mmol, 2 equiv.), remaining at 0 °C for 1 h and then stirred overnight at r.t. The resulting mixture was washed with CH_2Cl_2, concentrated under vacuum and purified by plate chromatography (SiO_2 eluted with 70:30 $CHCl_3$:MeOH) to afford 6,6′-dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose **3** as colorless solid (0.612 g, 63%). m.p. 73–75 °C.

$[\alpha]_D$ +41.0 (c 0.8, CH_3OH).

IR (KBr): ν_{max} 3377, 1720, 1636, 1570, 1053 cm^{-1}.

^1H NMR (400 MHz, D_2O): δ ppm 6.00 (s, 1H, =C$\underline{H}_{2a}$), 5.99 (s, 1H, =C$\underline{H}_{2a}$), 5.58 (s, 2H, =C$\underline{H}_{2b}$), 5.19 (d, J = 2.92 Hz, 1H, H-1), 4.13–3.99 (m, 5H, H-3′, H-6, H-6′), 3.83 (t, J = 8.06 Hz, 1H, H-4′), 3.77–3.65 (m, 2H, H-5, H-5′), 3.61 (t, J = 9.52 Hz, 1H, H-3), 3.57–3.44 (m, 3H, H-1′, H-2), 3.43–3.09 (m, 9H, H-4, 4× C$\underline{H}_2$), 1.77 (s, 6H, C$\underline{H}_3$).

^{13}C NMR (100 MHz, D_2O) δ 169.6, 169.5 (CO ester), 160.2, 160.1 (CO amide), 135.7, 135.7 (—$\underline{C}$(CH_3)=), 126.9 (=$\underline{C}H_2$), 103.7 (C-2′), 92.0 (C-1), 79.8 (C-5′), 76.6 (C-3′), 76.0 (C-4′), 72.1 (C-3), 71.6 (C-5), 71.2 (C-2), 71.1(C-4), 64.5 (C-6′), 64.4 (C-6), 61.3 (C-1′), 43.1 (—$\underline{C}H_2$), 40.9 (—$\underline{C}H_2$), 38.7 (—$\underline{C}H_2$), 17.4 ($\underline{C}H_3$).

MALDI-TOF MS: Calcd for $C_{26}H_{42}N_4O_{15}$ $[M+Na]^+$: 673.2544, Found 673.2539.

1′,2,3,3′,4,4′,6-Hepta-*O*-benzyl-6′-*O*-methanesulfonylsucrose **8**:

To a solution of 1′,2,3,3′,4,4′,6-hepta-*O*-benzylsucrose **7** (Barros et al., 2004) (1 g, 1.027 mmol) in CH_2Cl_2 (15 mL) under inert atmosphere was added Et_3N (0.158 mL, 1.13 mmol) and catalytic amount of 4-dimethylamino pyridine (DMAP). The reaction mixture was cooled to 0 °C in ice-water bath, then methanesulfonyl chloride (85 μL, 1.08 mmol) was added dropwise and reaction mixture was stirred for 30 min at 0 °C, followed by stirring at r.t. for 1.5 h. After completion of the reaction, reaction mixture was quenched with sat. solution of NH_4Cl and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude product, which was further purified by flash column chromatography (eluent, hexane/EtOAc; 4/1) to afford pure 1′,2,3,3′,4,4′,6-*O*-benzyl-6′-*O*-methanesulfonylsucrose **8** (95%, 1.028 g) as a viscous liquid.

IR (NaCl): ν_{max} 3030, 2912, 2867, 1496, 1454, 1359, 1208, 1176, 1090 cm^{-1}.

$[\alpha]_D$ +40.8 (c 1.0, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.30–7.12 (m, 35H, Ar) 5.59 (d, J = 3.2 Hz, 1H, H-1), 4.93–4.77 (m, 3H, PhC$\underline{H}_2$), 4.65–4.32 (m, 13H, 11H of PHC$\underline{H}_2$, 1H of H-6, H-3′), 4.23–4.17 (m, 2H, H-5′, H of 1H-1′), 4.10–3.94 (m, 3H, H-3, H-5, H-4′), 3.70 (d, J = 10.9, 1H, 1H of H-1′), 3.60–3.47 (m, 5H, H-2, H-4, H-6′, 1H of H-6), 2.88 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.7, 138.2, 138.1, 137.8, 137.6 (Ar-$\underline{C}_{quat}$), 128.3, 128.0, 127.8, 127.7, 127.6 (Ar), 104.8 (C-2′), 90.5 (C-1), 83.5 (C-3′), 81.8 (C-3, C-5, C-4′), 79.6 (C-2), 78.1 (C-5′), 77.6 (C-4), 75.5 ($\underline{C}H_2$), 74.9 ($\underline{C}H_2$), 73.3 ($\underline{C}H_2$), 72.9 ($\underline{C}H_2$), 72.7 ($\underline{C}H_2$), 70.8 (C-5), 70.4 (C-6), 70.2 (C-1′), 68.6 (C-6′), 37.1 (CH_3).

MALDI-TOF MS: Calcd for $C_{62}H_{66}O_{13}SNa$ $[M+Na]^+$): 1073.4122, found 1073.4116.

1′,2,3,3′,4,4′,6-Hepta-*O*-benzyl-6′-azido-6′-deoxysucrose **9**:

To a solution of 1′,2,3,3′,4,4′,6-*O*-benzyl-6′-*O*-methanesulfonylsucrose **8** (1 g, 0.95 mmol) in DMF (25 mL) was added NaN_3 (0.250 g, 3.8 mmol) and reaction mixture was subjected to microwave irradiation at 120 °C and 400 W for 10 min. After that the reaction was cooled to room temperature and quenched with water (30 mL), followed by extraction with Et_2O (3 × 20 mL). The organic layer was again washed with water (20 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (eluent, hexane/EtOAc; 4/1) to afford pure 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-azido-6′-deoxysucrose **9** (85%, 0.808 g) as colorless oil.

IR (NaCl): ν_{max} 3030, 2919, 2866, 2099, 1496, 1454, 1363, 1285, 1208, 1089 cm^{-1}.

$[\alpha]_D$ +42.2 (c 1.0, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.28–7.16 (m, 35H, ArH), 5.60 (d, J = 1.8 Hz, 1H, H-1), 4.90 (d, J = 10.7 Hz, 1H, PhC$\underline{H}_2$), 4.84–4.75 (m, 2H, PhC$\underline{H}_2$), 4.65–4.34 (m, 12H, H-3′, PhC$\underline{H}_2$), 4.10–3.94 (m, 4H, H-3, H-4′, H-5′, 1H of H-6), 3.69–3.43 (m, 7H, H-1′, H-2, H-4, H-5, 1H of H-6, 1H of H-6′), 3.17 (d, J = 12.3 Hz, 1H of H-6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.7, 138.4, 138.1, 138.0, 137.8, 137.7 (Ar-$\underline{C}_{quat}$), 128.3, 127.8, 127.7, 127.6, 127.5 (Ar), 104.6 (C-2′), 90.2 (C-1), 83.6 (C-3′), 82.9, 81.8, 79.6, 79.3, 77.8 (C-2, C-3, C-4, C-4′, C-5′), 75.5 (CH_2), 74.8 (CH_2), 73.4 (CH_2), 73.3 (CH_2), 72.8 (CH_2), 72.7 (CH_2), 72.6 (CH_2), 70.8 (C-6), 70.6 (C-5), 68.7 (C-1′), 53.6 (C-6′).

MALDI-TOF MS: Calcd for $C_{61}H_{63}N_3O_{10}Na$ $([M+Na]^+)$: 1020.4411, found 1020.4406.

1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-amino-6′-deoxysucrose **10**:

To a solution of 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-azido-6′-deoxysucrose **9** (0.500 g, 0.5 mmol) in THF:H_2O (5.5 mL; 10:1), was added Ph_3P (0.395 g, 1.5 mmol) and reaction mixture was heated at 70 °C for 3 h. The progress of reaction was monitored by TLC. After completion of the reaction (3 h), as indicated by disappearance of starting material and appearance of a new more polar spot on TLC, solvent was evaporated under reduced pressure to give crude product, which was purified by column chromatography on activated Al_2O_3 (eluent, 3% MeOH in CH_2Cl_2) to afford 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-amino-6′-deoxysucrose **10** (0.435 g, 89%) as colorless oil.

IR (NaCl): ν_{max} 3392, 3030, 2915, 2865, 1496, 1483, 1454, 1437, 1362, 1198, 1119, 1027 cm^{-1}.

$[\alpha]_D$ +41.1 (c 1.0, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.27–7.10 (m, 35H, ArH), 5.63 (d, J = 2.0 Hz, 1H, H-1), 4.90 (d, J = 10.8 Hz, 1H, PhC$\underline{H}_2$), 4.81–4.74 (m, 2H, PhC$\underline{H}_2$), 4.66–4.64 (m, 3H, PhC$\underline{H}_2$), 4.55–4.30 (m, 9H, 8H of PhC$\underline{H}_2$ and H-5′), 4.17–3.95 (m, 4H, H-3, H-3′, H-4′, H-5), 3.62–3.29 (m, 6H, H-2, H-1′, H-4, H-6), 3.07–2.96 (m, 2H, H-6′).

^{13}CNMR (100 MHz, $CDCl_3$): δ ppm 138.5, 138.0, 137.9, 137.8, 137.7, 137.2 (Ar-$\underline{C}_{quat}$), 128.5, 128.3, 127.8, 127.7, 127.6, 127.5 (Ar$\underline{C}$H), 104.7 (C-2′), 90.5 (C-1), 83.5 (C-3′), 82.1, 81.6, 79.3 (C-3, C-4′, C-5′), 78.5 (C-4), 77.8 (C-2), 75.5 ($\underline{C}H_2$), 74.9 ($\underline{C}H_2$), 73.4 ($\underline{C}H_2$), 73.3 ($\underline{C}H_2$), 73.1 ($\underline{C}H_2$), 72.7 ($\underline{C}H_2$), 72.4 ($\underline{C}H_2$), 71.4 (C-6), 71.0 (C-5), 69.1 (C-1′), 41.6 (C-6′).

MALDI-TOF MS: Calcd for $C_{61}H_{65}NO_{10}Na$ $([M+Na]^+)$: 994.4506, found 994.4501.

6′-Azido-6′-deoxy-sucrose **14**:

To a solution of 1′,2,3,3′,4,4′,6-hepta-*O*-acetyl-6′-azido-6′-deoxy-sucrose **13** (0.850 g, 1.285 mmol) in dry MeOH (15 mL) under Ar at r.t. was added NaOMe (0.345 g, 6.42 mmol) and the mixture was stirred at r.t. for 4 h. After completion of the reaction, reaction mixture was neutralized by passing through a short bed of Amberlite IR-120 (H^+-form), washed with dry MeOH and the filtrate was concentrated under reduced pressure to give crude product, which was purified by flash column chromatography (eluent; EtOAc/MeOH, 10/3) to afford 6′-azido-6′-deoxy-sucrose **14** (0.405 g, 85%) as colorless solid. m.p. 43–45 °C (EtOH) (not reported in literature) dec. 70 °C

$[\alpha]_D$ +64.8 (c 0.6, H_2O); Lit. (Singh et al., 1984) +68.0 (c 1.0, H_2O).

IR (KBr): ν_{max} 3391, 2924, 2105, 1656, 1637, 1281, 1136, 1053 cm^{-1}.

^1H NMR (400 MHz, D_2O): δ ppm 5.50 (d, J = 3.66 Hz, 1H, H-1), 4.11 (d, J = 8.5 Hz, 1H, H-3′), 3.98 (t, J = 8.40 Hz, 1H, H-4′), 3.83–3.88

(m, 1H, H-3), 3.76–3.78 (m, 2H, H-6), 3.63–3.70 (m, 3H, H-5, H-6′), 3.58 (s, 2H, H-1′), 3.43–3.48 (m, 2H, H-2 and H-5′), 3.33 (t, J = 9.36 Hz, 1H).

^{13}C NMR (100 MHz, D_2O): δ ppm 104.2 (C-2′), 92.5 (C-1), 80.0 (C-3), 76.5 (C-3′), 75.7 (C-4′), 72.8 (C-5, C-5′), 71.4 (C-2), 69.7 (C-4), 61.4 (C-1′), 60.7 (C-6), 53.2 (C-6′).

MALDI-TOF MS: Calcd for $C_{12}H_{21}N_3O_{10}$ $[M+Na]^+$: 390.3005, Found 390.1119.

6′-Amino-6′-deoxy-sucrose **15**:

To a solution of 6′-azido-6′-deoxy-sucrose **14** (0.367 g, 1 mmol) in dioxane: MeOH (10 mL, 8:2) at r.t. was added Ph_3P (1.05 g, 4 mmol) and the mixture was stirred at r.t. for 2 h. Then, NH_4OH (2.5 mL) was added and the mixture was stirred overnight. After completion of the reaction, as indicated by disappearance of starting material and appearance of a polar spot on TLC (eluent EtOAc/MeOH; 5/3), the solvent was evaporated under reduced pressure. The crude product was washed with EtOAc thrice and decanted. The residue was dissolved in water, filtered off and the filtrate was concentrated under reduced pressure to afford 6′-amino-6′-deoxy-sucrose **15** (0. 296 g, 86%) as faint pale yellow solid. m.p. 70–72 °C (H_2O); Lit. (Suami, Ikeda, Nishiyama, & Adaghi, 1975) 132–135 °C.

$[\alpha]_D$ + 58.8 (c 0.5, H_2O); Lit. (Singh et al., 1984) +57.3 (c 1.0, H_2O).

IR (KBr): ν_{max} 3446, 2924, 1654, 1457, 1340, 1138, 772 cm^{-1}.

^{1}H NMR (400 MHz, D_2O): δ ppm 5.29 (d, J = 3.69 Hz, 1H, H-1), 4.10 (d, J = 8.54 Hz, 1H, H-3′), 3.94 (t, J = 8.54 Hz, 1H, H-4′), 3.63–3.76 (m, 5H, H-3, H-5, H-5′, H-6), 3.56 (s, 2H, H-1′), 3.44 (dd, J = 3.66 and 10.24 Hz, 1H, H-2), 3.35 (t, J = 9.36 Hz, 1H, H-4), 2.87–2.89 (m, 2H, H-6′).

^{13}C NMR (100 MHz, D_2O): δ ppm 104.1 (C-2′), 92.6 (C-1), 81.3 (C-5′), 76.8 (C-3′), 75.6 (C-4′), 72.8 (C-5), 71.4 (C-2), 69.6 (C-4), 61.6 (C-1′), 60.5 (C-6), 43.2 (C-6′).

MALDI-TOF MS: Calcd for $C_{12}H_{23}NO_{10}$ $[M+Na]^+$: 364.1220, Found 364.1214.

Poly(*N*-(methacrylamido)-1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-amino-6′-deoxysucrose) **19**:

Homo-polymerization of monomer **1** (0.500 g, 0.48 mmol) was carried out in anhyd. toluene solution (0.1 M, 4.8 mL) in the presence of AIBN as radical initiator (1% by weight with respect to the monomer mixture, 5.0 mg). Dissolved oxygen was removed from the solutions by three freeze-thaw cycles on the vacuum pump. It was then heated at 70 °C until the polymerization was complete; the solution was cooled to r.t. and the product was precipitated in cold ethanol. The white solid was filtered and washed several times with cold ethanol. The polymer was purified by repeated dissolution in toluene and reprecipitation in cold ethanol and dried under vacuum to yield 0.070 g, 14% of polymer **19** as white powder.

Poly(*N*-(methacrylamido)-1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-amino-6′-deoxysucrose)-co-polystyrene **20**:

Co-polymerization of monomer **1** (0.500 g, 0.48 mmol) with styrene (10 equiv., 0.55 mL, 4.80 mmol) was carried out in anhyd. toluene solution (0.1 M, 4.8 mL) in the presence of AIBN as radical initiator (1% by weight with respect to the monomer mixture, 10 mg). Dissolved oxygen was removed from the solutions by three freeze-thaw cycles on the vacuum pump. It was then heated at 70 °C until the polymerization was complete, the solution was cooled to r.t. and the product precipitated in cold ethanol. The white solid was filtered and washed several times with cold ethanol. The polymer was purified by repeated dissolution in toluene and reprecipitation in cold ethanol and dried under vacuum to yield 0.480 g, 48% of polymer **20** as white powder.

Poly(6,6′-dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose) **21**:

Polymer **21** synthesis was carried out by dissolving **2** (0.500 g, 1.01 mmol) in dist. H_2O (0.1 M, 10 mL), and the solution was sparged with Ar for 15 min. Sodium persulfate (1%, 5 mg) was added, and the solution was stirred at 70 °C for 24 h. The resulting polymer was recovered by filtration, washed with methanol and dried under vacuum. The polymer **21** was obtained in 18% recovered yield (0.09 g) and was characterized as amorphous solid.

Poly(6,6′-dideoxy-6,6′-*N*-dimethacryloyloxy ethylureido sucrose)-co-polystyrene **22**:

Co-polymerization of monomer **2** (0.500 g, 1.01 mmol) with styrene (10 equiv., 1.15 mL, 10.1 mmol) was carried out in anhydrous DMF solution (0.1 M, 10 mL) in the presence of AIBN as radical initiator (1% by weight with respect to the monomer mixture, 15 mg). Dissolved oxygen was removed from the solutions by three freeze-thaw cycles on the vacuum pump. It was then heated at 70 °C until the polymerization was complete, the solution was cooled to r.t. and the product precipitated in cold ethanol. The white solid was filtered and washed several times with cold acetone. The polymer **22** was dried under vacuum to yield 0.217 g, 14% as white amorphous powder.

Poly(6,6′-dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose) **23**:

Homo-polymeric hydrogel **23** synthesis was carried out by dissolving **3** (0.500 g, 0.769 mmol) in dist. H_2O (0.1 M, 8 mL), and the solution was sparged with Ar for 15 min. Sodium persulfate (1%, 5 mg) was added, and the solution was stirred at 70 °C for 24 h. The resulted heterogeneous mixture was filtered and washed thoroughly with dist. water and then cold methanol to remove any residual monomer, then dried under vacuum to yield **23** as insoluble amorphous powder (0.250 g, 20%).

Poly(6,6′-dideoxy-6,6′-*N*-dimethacryloyloxyethylureido sucrose)-co-polystyrene **24**:

Monomer **3** (0.500 g, 0.769 mmol) was dissolved in dist. H_2O (0.1 M, 8 mL) and sodium persulfate (1%, 5 mg) was added. Styrene (10 equiv., 0.88 mL, 7.69 mmol) was dissolved in toluene (8 mL). The two solutions were combined and sparged with Ar for 15 min; then heated at 70 °C for 24 h while stirred vigorously. The resulted heterogeneous mixture was filtered and washed thoroughly with dist. water and then cold methanol to remove any residual monomer, then dried under vacuum to yield **24** as insoluble amorphous powder (0.689 g, 53%).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.03.050.

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