Syntheses of Optically Active Monomers and Copolymers Derived from Protected 6′-*O*-Acryloyl Sucroses

M. Teresa Barros,* Fernando Siñeriz

Departamento de Química, Centro de Química Fina e Biotecnologia, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal
Fax +351(21)2948550; E-mail: mtbarros@dq.fct.unl.pt
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Abstract: Selectively 6′-*O*-monoacrylated monomers of fully protected sucrose moieties were synthesized by a multistep route. Chiral copolymers were prepared from these monomers with styrene or methyl methacrylate using radical initialization with azobisisobutyronitrile (AIBN). The quantitative incorporation of substoichiometric components was verified. Copolymers composition and purity were reliably analyzed by ^{1}H NMR and SEC.

Key words: carbohydrates, monoacrylates, regioselectivity, free radical polymerization, polymers

Vinyl sugars can be easily copolymerized with various comonomers and constitute polymers of a special structural type. They have potential for modifying and improving several properties of conventional polymer materials namely the introduction of chirality, superior biodegradability and biocompatibility.[1,2] Extensive studies on the syntheses of vinyl monomers and polymers of saccharides have been reported.[3–7]

The most common approach to these compounds, in order to attain the monomer susceptible to polymerization, is by the attachment of an unsaturated component to the sugar. This linkage is usually in the form of an ether, ester or amido group.[4]

In the context of the use of sucrose as a chemical raw material[8,9] there is an increasing interest in this chemistry field[10,11] and several studies in this area can be found during the last decade.[8,12,13]

The hydroxyl positions where the vinyl group has been regioselectivity introduced in the sucrose molecule have traditionally been the primary hydroxyl or the 4-OH on the glucose moiety[12,13]or the 1′-OH of the fructose moiety.[9,14]A high degree of regioselectivity can be achieved by the enzymatic approach[9,14] although some disadvantages and limitations can be found in the use of enzymes (low stability of the enzymes in organic solvents or the correct choice of agents for introducing the unsaturation).[11] To our knowledge, ester sucrose monomers have never been prepared chemically at the 6′-*O* position for building vinyl polymers.

Several strategies have been employed to obtain sucrose with the 6′-OH free for functionalization.[15–20] We have developed[21] a multistep procedure[22] that allowed us to obtain selectively the unprotected 6′-hydroxyl and we have prepared vinyl sucrose derivatives from this intermediate. Using this strategy, we were able to control the regioselective monofunctionalization of the sugar in order to form a monomer which could be converted into pure linear polymers, avoiding the presence of mixtures of mono- and (or) multi-substituted modified sucrose molecules that results in cross-linked polymerization.[2,11]

The properties of these polymers are dependent on the diverse substituents on the sugar,[1] and we have prepared several sucrose monomers protected with different groups. These sugar monomers, containing a unique polymerizable double bond, were subjected to free-radical polymerization using azobisisobutyronitrile (AIBN) affording optically active copolymers.

Here we report the selective preparation of three new 6′-*O*-methacryloyl esters of protected sucroses and the synthesis of new crotonyl derivatives monomers of sucrose. The study of the copolymerization of one monomer with styrene or methyl methacrylate as well as the characterization of the corresponding sucrose polymers is also described.

The first step to our targets consisted in a regioselective silylation of the 6′-hydroxyl group (Scheme 1) of the sucrose using *tert*-butyldiphenylchlorosilane (TBDPSCl) according to the methods described earlier,[22] followed by an acylation or alkylation of the remaining hydroxyl groups.

The monosilylated sucrose **1**[22] was reacted with three different agents, namely methyl iodide (MeI), benzoyl chloride (BzCl) and 3,4,5-tri-*O*-methylgalloyl chloride, leading respectively to the compounds **2**,**3**,[22] and **4**. Because of a slight instability of the TBDPS protecting group under strongly basic conditions (KOH, DMSO), required for the alkylation,[23] we have always obtained the expected octamethylsucrose as a byproduct during the preparation of **2**. Good yields have been obtained in the acylation step for the synthesis of **3** in the presence of 4-dimethylaminopyridine (4-DMAP), or in the presence of tetramethylethylenediamine (TMEDA) for the synthesis of **4**.[21,24] To prepare this latter product, it has been necessary to heat at reflux temperature in order to protect all the hydroxyl groups, otherwise the hexaacylated sugar was isolated, being unprotected at the 2-OH.

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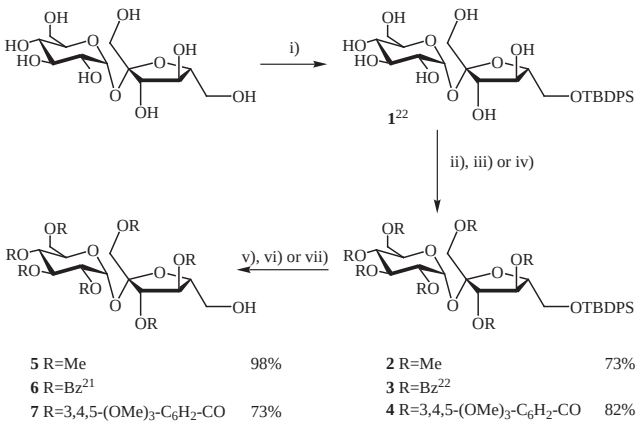


5 R=Me 98%
6 R=Bz[21]
7 R=3,4,5-(OMe)$_3$-C$_6$H$_2$-CO 73%

1[22]

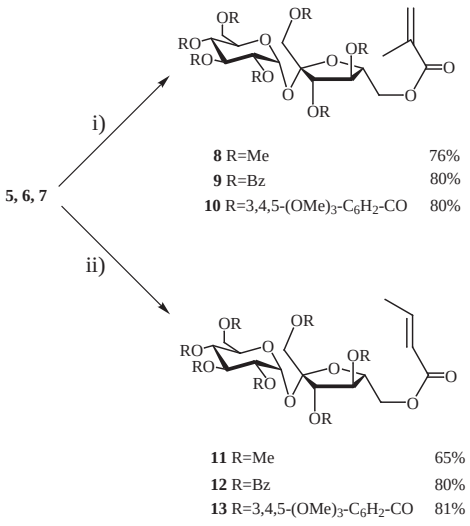
2 R=Me 73%
3 R=Bz[22]
4 R=3,4,5-(OMe)$_3$-C$_6$H$_2$-CO 82%

Scheme 1 i) TBDPSCI, py; ii) MeI, KOH, DMSO, 73%; iii) BzCl, py, DMAP; iv) 3,4,5-(OMe)$_3$-C$_6$H$_2$COCl, MeCN, TMEDA, 82%; v) Bu_4NF, THF, 98%; vi) 1% Br_2/MeOH; vii) 0.1% Br_2/MeOH, 73% + 22% initial

Selective deprotection of the silyl group, with TBAF at room temperature or with Br_2/MeOH at reflux, furnished, compounds **5**,**6**,[21] and **7** (73% yield, 22% of the starting material was recovered), respectively, from **2**,**3** and **4**, after column chromatography. In the case of **6** or **7** migrations of the acyl groups were avoided by the use of bromine (Br_2) in methanol (MeOH) at reflux, a recently developed methodology.[25]

Esterification reactions of the 6′-hydroxyl free sucrose were carried out by treating the sugars **5**–**7**, in dichloromethane in the presence of triethylamine at room temperature with the appropriate anhydride as reagent, to give the expected compounds **8**–**13** (Scheme 2) in good yields.

Some problems were encountered in the purification of the monomers, particularly in the case of **13**, where traces of impurities were difficult to separate from the required compound.



8 R=Me 76%
9 R=Bz 80%
10 R=3,4,5-(OMe)$_3$-C$_6$H$_2$-CO 80%

11 R=Me 65%
12 R=Bz 80%
13 R=3,4,5-(OMe)$_3$-C$_6$H$_2$-CO 81%

Scheme 2 i) methacrylic anhydride, Et_3N, CH_2Cl_2, DMAP; ii) crotonic anhydride, Et_3N, CH_2Cl_2, DMAP

In the ^{1}H NMR spectra of all these compounds two signals have been attributed to the double bond: singlet at 6.14 ppm and triplet at 5.55 ppm for the compounds with the methacrylic moiety (**8**,**9** and **10**); and for those compounds with the crotonic moiety (**11**,**12** and **13**) a double quadruplet or multiplet at 6.93 ppm and a doublet at 5.80 ppm. We could also assign the allylic methyl groups of the molecules at 1.90 ppm (s for **8**–**10**) and 1.75 ppm (d for **11**–**13**). The presence of a signal at about 18 ppm in each of the homodecoupled ^{13}C NMR spectra of these six compounds, confirmed the presence of the new methyl group.

The polymerizability (homo- and copolymerization) of monomer **9** has been examined in the presence of AIBN as free-radical initiator in toluene at 70 °C. Unfortunately, homopolymerization of compound **9** failed to give polymers of high molar mass as did the copolymerization with acrylonitrile. We found that copolymerization of compound **9** (Table) with styrene or methyl methacrylate afforded the expected poly(sucrose 6′-acrylate) after 24 hours of reaction and precipitation with ethanol (0 °C). A study of the effect of varying the stoichiometry of the comonomers on the sugar incorporation in the final copolymers has been carried out. As a result, we obtained several copolymers with diverse degrees of protected sucrose appended. This resulted in different physical properties such as optical rotations. As expected this lowered progressively with the larger participation of the non-optically active comonomer.

Poly(sucrosyl) composition has been determined from the ^{1}H NMR spectra of the copolymers. The structures have been verified by comparing the peak areas of both the methylene and methyl protons of the polymer chain (0.8–2.2 ppm), as well as the methoxy protons, when the comonomer is methyl methacrylate, with the 14 protons area of the sucrose units. We have noticed in the ^{13}C NMR spectrum of the copolymer with methyl methacrylate, the presence of two different groups of carbonyl signals, one from the sugar ester moiety and the other from the carbonyls of the comonomer.

Data obtained by Size Exclusion Chromatography (SEC) analysis, revealed monomodal distributions. Copolymer molecular weights (*Mw*), estimated by the same method, were in a similar range of values to those of similar copolymers.[8,12] Polydispersity values (*Mw/Mn*) revealed a certain degree of heterogeneity under the adopted conditions of work. Copolymers were soluble in classical organic solvents and insoluble in water as would be expected for a fully capped sugar.

In summary, some 6′-hydroxyl free (otherwise protected) sucrose derivatives have been prepared. Selective incorporation of unsaturated ester groups for the preparation of sucrose monomers was accomplished through its reaction with the corresponding symmetrical anhydrides in the presence of DMAP as catalyst. As a final point, new chiral copolymers containing sucrose were synthesized by radical polymerization and some of their physical properties were determined.

Table Copolymerization of **9** with Styrene or Methyl Methacrylate in the Presence of Radical Initiator AIBN (toluene, 70 °C, 24 h)

Alkene	$\frac{[9]_O}{[C]_O}$ [a]	$\frac{[9]}{[C]}$ [b]	Yield (%)	M_w [c]	$\frac{M_w}{M_n}$	$[\alpha]_D$ [d]
styrene	0.25	0.017	51	10763	2.67	+ 8.4 (*c* = 1.0, $CHCl_3$)
methyl methacrylate	1	0.091	84	9670	2.23	+22.7 (*c* = 1.5, $CHCl_3$)
methyl methacrylate	0.50	0.083	65	11970	1.62	+21.1 (*c* = 1.6, $CHCl_3$)
methyl methacrylate	0.25	0.063	83	18127	1.62	+17.0 (*c* = 1.0, $CHCl_3$)

[a] Initial molar ratio of monomers.
[b] Mole ratio of comonomer units in copolymer, determined by ^{1}H NMR.
[c] Determined by SEC with DMF as solvent using polyethyleneglycols as standards.
[d] Monomer **9**: $[\alpha]_D$ +37.8 (*c* = 1.1, $CHCl_3$).

Reagents and solvents were purified before use.[26] All reactions were run under a positive pressure of dry argon except for the preparation of **2**,**6** and **7**. Flash chromatography was performed on silica gel (Macherey-Nagel Kieselgel 60 M). Preparative TLC was performed on glass plates coated with 1 mm of silica gel (Macherey-Nagel, Kieselgel DGF_{254}). Analytical TLC: Aluminum-backed silica gel (Merck 60 F_{254}). Optical rotations were measured at 20 °C on an AA-1000 polarimeter (0.5 dm cell). NMR spectra were recorded on a Bruker AMX-400 spectrometer (^{1}H at 400 MHz and ^{13}C at 100 MHz) in $CDCl_3$with chemical shift values (δ) in ppm downfield from TMS. Some compound signals were assigned by performing additional ^{1}H-^{1}H COSY and HMQC measurements on the same spectrometer. SEC analyses were performed on a Knauer apparatus supplied with two columns PL Gel Mixed (5 μm) and pre-column PL Gel; oven Eldec LH-150 and a refraction index detector. The equipment was calibrated with polyethyleneglycol standards. Determinations were run at 70 °C using a flow of 1 mL/min for a concentration of the sample in DMF of 1% (w/w). Microanalyses were performed by the IST analytical services in Lisbon using a combustion apparatus.

6′-*O*-*tert*-Butyldiphenylsilyl-2,3,4,6,1′,3′,4′-hepta-*O*-methylsucrose (2)

To a suspension of KOH (2.70 g, 28.0 equiv, 48.2 mmol) in DMSO (4 mL) at r.t. was added, after 30 min, compound **1**[22] (1.00 g, 1.7 mmol), immediately followed by MeI (1.50 mL, 14.0 equiv, 24.1 mmol). The mixture was stirred for an additional 10 min. Then, H_2O (10 mL) was added and several extractions with CH_2Cl_2 (5 × 15 mL) were performed. The combined organic layers were dried (Na_2SO_4), and the solvent was evaporated to afford a pale yellow oil that was purified by flash column chromatography (EtOAc–hexane, 1:1) to yield 0.85 g (73%) of **2**; $[\alpha]_D$ +41.5 (*c* = 1.5, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 7.67 (m, 4 H, Ar), 7.38 (m, 6 H, Ar), 5.56 (d, 1 H, *J* = 3.6 Hz, H-1), 4.04 (t, 1 H, *J* = 7.2 Hz, H-3′), 3.90 (t, 1 H, *J* = 7.2 Hz, H-4′), 3.89 (t, 1 H, *J* = 7.2 Hz, H-5′), 3.88 (m, 2 H, 2 H-6′), 3.84 (m, 1 H, H-5), 3.60 (m, 1 H, H-1′a), 3.56, 3.51, 3.47, 3.44, 3.41, 3.39, 3.28 (7 s, 21 H, 7 CH_3O), 3.49 (m, 1 H, H-6a), 3.38 (m, 1 H, H-3), 3.36 (m, 1 H, H-1′a), 3.33 (m, 1 H, H-6b), 3.18 (t, 1 H, *J* = 9.6 Hz, H-4), 3.05 (dd, 1 H, *J* = 9.6, 3.6 Hz, H-2), 1.05 (s, 9 H, *t*-C_4H_9).

^{13}C NMR ($CDCl_3$): δ = 19.04 (*C*Me_3), 26.63 [C(*C*H_3)$_3$], 57.91, 58.25, 58.52, 58.99, 59.36, 60.06, 60.49 (7 CH_3O), 64.96 (C-6′), 70.25 (C-5), 70.92 (C-6), 74.18 (C-1′), 79.20 (C-4), 80.83 (C-5′), 81.41 (C-2), 83.00 (C-3), 84.15 (C-4′), 85.60 (C-3′) 89.01 (C-1), 104.07 (C-2′), 127.71–135.70 (Ar).

Anal. Calcd for $C_{35}H_{54}O_{11}Si$ (678.34): C, 61.92; H, 8.02. Found: C, 61.92; H, 8.18.

6′-*O*-*tert*-Butyldiphenylsilyl-2,3,4,6,1′,3′,4′-hepta-*O*-(tri-*O*-methylgalloyl)sucrose (4)

To compound **1** (0.40 g, 0.7 mmol) in MeCN (10 mL) was added TMEDA (1.17 mL, 0.90 g, 7.7 mmol) under stirring. The mixture was cooled to 0 °C and a solution of tri-*O*-methylgalloyl chloride (1.78 g, 7.7 mmol) in MeCN (5 mL) was added. The temperature was allowed to rise, then stirred overnight at reflux. After neutralization by a solution of phosphate buffer (pH 7, 35 mL), a white precipitate appeared. The precipitate was filtered off and washed with H_2O (15 mL). Flash chromatography (EtOAc–hexane, 2:1) of the remaining solid yielded **4** (1.10 g, 82%) as a white powder; $[\alpha]_D$ +23.3 (*c* = 1.2, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 7.69 (m, 4 H, Ar), 7.32–6.98 (7 s, 14 H, Ar), 7.31 (m, 6 H, Ar), 6.27 (m, 2 H, H-1, H-4′), 6.02 (t, 1 H, *J* = 10.0 Hz, H-3), 5.84 (d, 1 H, *J* = 7.6 Hz, H-3′), 5.74 (t, 1 H, *J* = 10.0 Hz, H-4), 5.31 (dd, 1 H, *J* = 10.2, 3.6 Hz, H-2), 4.75 (d, 1 H, *J* = 11.8 Hz, H-1′a), 4.57 (d, 1 H, *J* = 10.0 Hz, H-5), 4.50 (d, 1 H, *J* = 11.6 Hz, H-1′b), 4.32 (ddd, 1 H, *J* = 7.6, 4.4, 4.2 Hz, H-5′), 4.10 (m, 4 H, 2 H-6 and 2 H-6′), 3.93–3.76 (11 s, 63 H, 21 CH_3O), 1.01 (s, 9 H, *t*-C_4H_9).

^{13}C NMR ($CDCl_3$): δ = 19.72 (*C*Me_3), 27.29 [C(*C*H_3)$_3$], 56.69–56.93 (*C*H_3OAr), 61.51 (*C*H_3OAr), 63.33, 63.76, 66.78 (C-6, C-1′ and C-6′), 69.54, 70.09, 71.53, 72.09 (C-2, C-3, C-4 and C-5), 74.62, 78.60 (C-3′ and C-4′), 81.09 (C-5′), 90.30 (C-1), 104.18 (C-2′), 107.75–153.68 (Ar), 165.52, 165.69, 165.86, 166.86, 166.03, 166.24 (7 CO).

Anal. Calcd for $C_{98}H_{110}O_{39}Si$ (1940.03): C, 60.67; H, 5.71. Found: C, 60.68; H, 5.81.

2,3,4,6,1′,3′,4′-Hepta-*O*-methylsucrose (5)

To a solution of **2** (0.75 g, 1.1 mmol) under argon was added a 1.0 M solution of TBAF in THF (2.22 mL, 2.2 mmol). After stirring for 4 h, TLC (EtOAc) showed no traces of the starting material. Evaporation of the solvent followed by purification on silica gel (EtOAc) gave the title compound **5** (0.49 g, 98%); $[\alpha]_D$ +46.7 (*c* = 1.3, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 5.46 (d, 1 H, *J* = 3.6 Hz, H-1), 4.07 (m, 1 H, H-3′), 4.04 (m, 1 H, H-4′), 3.93 (m, 1 H, H-5′), 3.89 (m, 1 H, H-5), 3.85 (m, 2 H, 2 H-6′), 3.62, 3.53, 3.50, 3.49, 3.48, 3.42, 3.40 (7 s, 21 H, 7 CH_3O), 3.62–3.40 (m, 5 H, H-3, 2 H-6 and 2 H-1′), 3.28 (t, 1 H, *J* = 9.6 Hz, H-4), 3.14 (dd, 1 H, *J* = 9.6, 3.6 Hz, H-2).

^{13}C NMR ($CDCl_3$): δ = 58.95, 59.25, 59.39, 59.83, 60.10, 61.05, 61.32, (7 CH_3O), 62.01 (C-6′), 70.93 (C-5), 71.67 (C-6), 74.77 (C-1′), 79.56 (C-4), 81.64 (C-5′), 81.98 (C-2), 82.13 (C-3), 83.63 (C-4′), 85.78 (C-3′), 91.13 (C-1), 104.16 (C-2′).

2,3,4,6,1′,3′,4′-Hepta-*O*-(tri-*O*-methylgalloyl)sucrose (7)
Compound **4** (1.00 g, 0.5 mmol) was refluxed in a 0.1% (w/w) solution of Br_2 in MeOH (82 mL) for 6 h. Then, the mixture was cooled and the excess of Br_2 was destroyed by a solution of aq 5% $Na_2S_2O_3$ (20 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic layers were dried (Na_2SO_4), concentrated, and the residue was purified on silica gel (EtOAc–hexane, 2:1) to give **7** (0.64 g, 73%); $[\alpha]_D$ +14.1 (*c* = 0.8, $CHCl_3$). Unchanged starting material **4** (0.22 g, 22%) was also recovered.

^{1}H NMR ($CDCl_3$): δ = 7.39–7.06 (7 s, 14 H, Ar), 6.27 (d, 1 H, *J* = 3.2 Hz, H-1), 6.01 (t, 1 H, *J* = 10.0 Hz, H-3), 5.96 (m, 2 H, H-3′ and H-4′), 5.74 (t, 1 H, *J* = 10.0 Hz, H-4), 5.16 (dd, 1 H, *J* = 10.2, 3.6 Hz, H-2), 4.66 (d, 1 H, *J* = 11.6 Hz, H-1′a), 4.58 (d, 1 H, *J* = 11.6 Hz, H-1′b), 4.56 (m, 1 H, H-5), 4.20–4.01 (m, 5 H, 2 H-6, H-5′ and 2 H-6′), 3.93–3.76 (11 s, 63 H, 21 CH_3O), 1.26 (br s, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 56.67 (*C*H_3OAr), 61.35 (*C*H_3OAr), 62.13, 63.28, 65.31 (C-6, C-1′ and C-6′), 69.53, 69.81, 71.81, 72.50 (C-2, C-3, C-4 and C-5), 75.09, 78.29 (C-3′ and C-4′), 82.26 (C-5′), 94.17 (C-1), 103.71 (C-2′), 107.54–153.38 (Ar), 165.60, 165.79, 165.90, 166.00, 166.40, 166.51, 167.08 (7 CO).

Synthesis of Monomers; General Procedure
To a 0.1 M solution of the 6′-OH free sugars **5**–**7** in anhyd CH_2Cl_2 was added Et_3N (2.5 equiv) and a catalytic amount of 4-DMAP. The mixture was cooled at 0 °C, and then a 0.5 M solution of methacrylic anhydride or crotonic anhydride (*cis*/*trans* mixture) (1.2 equiv) in anhyd CH_2Cl_2 was added. The reaction mixture was allowed to warm until r.t. When no more starting material remained, the mixture was diluted with more CH_2Cl_2 (5 × 15 mL per mmol of starting material) and washed with aq 1.0 M HCl (15 mL per mmol of starting material), H_2O (15 mL per mmol starting material), sat. aq $NaHCO_3$ (15 mL per mmol starting material) and brine (15 mL per mmol starting material). The organic layer was dried (Na_2SO_4) and the solvent was evaporated. Purification of the crude by flash chromatography led to the expected products **8**–**13**.

6′-*O*-(Methacryloyl)-2,3,4,6,1′,3′,4′-hepta-*O*-methylsucrose (8)
The reaction of **5** (0.79 g, 1.8 mmol) with of methacrylic anhydride (0.32 mL, 2.2 mmol) was carried out according to the general procedure during 24 h. Purification by column chromatography on silica gel (EtOAc–hexane, 3:1) afforded 0.69 g (76%) of **8**; $[\alpha]_D$ +49.9 (*c* = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 6.14 (s, 1 H, H-βa), 5.57 (t, 1 H, *J* = 1.6 Hz, H-βb), 5.50 (d, 1 H, *J* = 3.4 Hz, H-1), 4.39 (m, 2 H, 2 H-6′), 4.05 (m, 1 H, H-3′), 4.03 (t, 1 H, *J* = 7.5 Hz, H-5′), 3.93 (m, 1 H, H-5), 3.89 (t, 1 H, *J* = 7.5 Hz, H-4′), 3.62 (m, 1 H, H-1′a), 3.61, 3.54, 3.48, 3.46, 3.44, 3.42, 3.40 (7 s, 21 H, 7 CH_3O), 3.59 (m, 2 H, 2 H-6), 3.57 (m, 1 H, H-3), 3.53 (m, 1 H, H-1′b), 3.19 (dd, 1 H, *J* = 10.0, 9.6 Hz, H-4), 3.13 (dd, 1 H, *J* = 9.7, 3.6 Hz, H-2), 1.94 (s, 3 H, C*H*$_3$CH=CH).

^{13}C NMR ($CDCl_3$): δ = 18.00 (*C*H_3CH=CH_2), 58.16, 58.26, 58.32, 59.91, 59.18, 60.07, 60.41 (7 CH_3O), 65.70 (C-6′), 70.30 (C-5), 70.96 (C-6), 73.53 (C-1′), 78.06 (C-5′), 79.25 (C-4), 81.45 (C-2), 82.92 (C-3), 83.99 (C-4′), 84.92 (C-3′), 89.27 (C-1), 104.21 (C-2′), 125.76 (CH$_3$CH=*C*H$_2$), 136.05 (CH$_3$*C*H=CH$_2$), 167.13 (CO).

Anal. Calcd for $C_{23}H_{40}O_{12}$ (508.56): C, 54.32; H, 7.93. Found: C, 54.37; H, 8.02.

6′-*O*-(Methacryloyl)-2,3,4,6,1′,3′,4′-hepta-*O*-benzoylsucrose (9)
The reaction of **6** (1.08 g, 1.0 mmol) with methacrylic anhydride (0.18 mL, 1.2 mmol) was carried out according to the general procedure during 1.5 h. Chromatographic purification (silica gel, EtOAc–hexane, 1:2) afforded 0.92 g (80%) of **9**; $[\alpha]_D$ +37.8 (*c* = 1.1, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 8.20–7.14 (m, 35 H, Ar), 6.21 (t, 1 H, *J* = 10.0 Hz, H-3), 6.15 (d, 1 H, *J* = 3.4 Hz, H-1), 6.14 (s, 1 H, H-βa), 5.97 (d, 1 H, *J* = 5.5 Hz, H-3′), 5.93 (t, 1 H, *J* = 5.5 Hz, H-4′), 5.78 (t, 1 H, *J* = 9.9 Hz, H-4), 5.50 (s, 1 H, H-βb), 5.44 (dd, 1 H, *J* = 10.4, 3.5 Hz, H-2), 4.71 (d, 1 H, *J* = 11.9 Hz, H-1′a), 4.70 (m, 1 H, H-5 or H-5′), 4.60 (d, 1 H, H-1′b), 4.52 (s, 2 H, 2 H-6), 4.47–4.45 (m, 2 H, H-5 or H-5′ and H-6′a), 4.35 (dd, 1 H, *J* = 12.5, 3.0 Hz, H-6′b), 1.89 (s, 3 H, C*H*$_3$CH=CH$_2$).

^{13}C NMR ($CDCl_3$): δ = 18.04 (*C*H_3CH=CH$_2$), 62.23, 63.60, 64.92 (C-6, C-1′ and C-6′), 68.95, 69.12, 70.03, 71.25 (C-2, C-3, C-4 and C-5), 76.05, 77.53 (C-3′ and C-4′), 78.96 (C-5′), 90.77 (C-1), 104.60 (C-2′), 126.40, 128.29–135.76 (Ar and *C*H=*C*H$_2$), 165.20, 165.46, 165.50, 165.66, 165.91, 166.14, 166.92 (8 CO).

Anal. Calcd for $C_{65}H_{54}O_{19}$ (1139.11): C, 68.54; H, 4.78. Found: C, 68.68; H, 4.77.

6′-*O*-(Methacryloyl)-2,3,4,6,1′,3′,4′-hepta-*O*-(tri-*O*-methylgalloyl)sucrose (10)
The reaction of **7** (0.17 g, 0.1 mmol) with methacrylic anhydride (17.8 μL, 0.1 mmol) was carried out according to the general procedure during 30 min. Chromatographic purification (silica gel, EtOAc–hexane, 2:1) afforded 0.14 g (80%) of **10**; $[\alpha]_D$ +17.7 (*c* = 0.7, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 7.35–7.02 (7 s, 14 H, Ar), 6.22 (d, 1 H, *J* = 3.6 Hz, H-1), 6.11 (s, 1 H, H-βa), 5.96 (t, 1 H, *J* = 10.0 Hz, H-3), 5.92 (t, 1 H, *J* = 4.8 Hz, H-3′), 5.81 (t, 1 H, *J* = 10.0 Hz, H-4′), 5.70 (t, 1 H, H-4), 5.53 (s, 1 H, H-βb), 5.20 (dd, 1 H, *J* = 11.2, 3.6 Hz, H-2), 4.82–4.51 (m, 7 H, H-5, H-6a, 2 H-1′, H-5′, 2 H-6′), 4.20 (dd, 1 H, *J* = 13.8, 3.4 Hz, H-6b), 3.92–3.69 (12 s, 63 H, 21 CH_3O), 1.87 (s, 3 H, C*H*$_3$CH=CH$_2$).

^{13}C NMR ($CDCl_3$): δ = 18.86 (*C*H_3CH=CH$_2$), 56.57–56.96 (*C*H_3OAr), 61.53 (*C*H_3OAr), 63.17, 64.27, 65.66 (C-6, C-1′ and C-6′), 69.88, 70.04, 71.18, 72.70 (C-2, C-3, C-4 and C-5), 77.16, 78.01 (C-3′ and C-4′), 80.41 (C-5′), 91.54 (C-1), 105.97 (C-2′), 107.56–153.76 (Ar and *C*H=*C*H$_2$), 165.52, 165.60, 165.87, 165.92, 166.31, 167.43 (8 CO).

Anal. Calcd for $C_{86}H_{96}O_{40}$ (1769.70): C, 58.37; H, 5.47. Found: C, 58.62; H, 5.89.

6′-*O*-(Crotonyl)-2,3,4,6,1′,3′,4′-hepta-*O*-methylsucrose (11)
The reaction of **5** (0.50 g, 1.1 mmol) with crotonic anhydride (0.20 mL, 1.4 mmol) was carried out according to the general procedure during 24 h. Chromatographic purification (silica gel, EtOAc–hexane, 3:1) afforded 0.38 g (65%) of **11**; $[\alpha]_D$ +59.7 (*c* = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 6.93 (dq, 1 H, *J* = 15.2, 6.8 Hz, H-β), 5.80 (d, 1 H, *J* = 15.4, H-α), 5.44 (d, 1 H, *J* = 3.6 Hz, H-1), 4.29 (m, 2 H, 2 H-6′), 3.96 (m, 1 H, H-3′), 3.93 (m, 1 H, H-5′), 3.85 (m, 1 H, H-5), 3.80 (t, 1 H, *J* = 7.6 Hz, H-4′), 3.54, 3.46, 3.41, 3.39, 3.36, 3.34, 3.32 (7 s, 21 H, 7 CH_3O), 3.52 (m, 1 H, H-1′a), 3.51 (m, 2 H, 2 H-6), 3.40 (m, 1 H, H-3), 3.34 (m, 1 H, H-1′b), 3.12 (t, 1 H, *J* = 9.6 Hz, H-4), 3.05 (dd, 1 H, *J* = 9.4, 3.7 Hz, H-2). 1.81 (d, 3 H, 6.4 Hz, C*H*$_3$CH=CH).

^{13}C NMR ($CDCl_3$): δ = 17.77 (*C*H_3CH=CHCO), 58.17, 58.33, 58.94, 59.19, 60.09, 60.45 (7 CH_3O), 65.31 (C-6′), 70.27 (C-5), 70.95 (C-6), 73.55 (C-1′), 78.13 (C-5′), 79.23 (C-4), 81.46 (C-2), 82.90 (C-3), 83.70 (C-4′), 84.91 (C-3′), 89.22 (C-1), 104.04 (C-2′), 122.25 (CH$_3$CH=*C*H), 144.89 (CH$_3$*C*H=CH), 165.97 (CO).

Anal. Calcd for $C_{23}H_{40}O_{12}$ (508.56): C, 54.32; H, 7.93. Found: C, 54.22; H, 8.02.

6′-*O*-(Crotonyl)-2,3,4,6,1′,3′,4′-hepta-*O*-benzoylsucrose (12)

The reaction of **6** (0.50 g, 0.5 mmol) with crotonic anhydride (83.5 μL, 0.6 mmol) was carried out according to the general procedure during 1.5 h. Chromatographic purification (silica gel, EtOAc–hexane, 1:2) afforded 0.43 g (80%) of **12**; $[\alpha]_D$ +33.0 (*c* = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 8.21–7.12 (m, 35 H, Ar), 6.95 (dq, 1 H, *J* = 15.6, 6.8 Hz, H-β), 6.24 (t, 1 H, *J* = 5.0 Hz, H-3), 6.15 (d, 1 H, *J* = 3.2 Hz, H-1), 5.97 (d, 1 H, *J* = 5.6 Hz, H-3′), 5.91 (t, 1 H, *J* = 5.6 Hz, H-4′), 5.83 (d, 1 H, *J* = 15.6 Hz, H-α), 5.79 (t, 1 H, *J* = 9.4 Hz, H-4), 5.45 (dd, 1 H, *J* = 10.6, 3.4 Hz, H-2), 4.73 (m, 2 H, H-1′a and H-5or H-5′), 4.61 (d, 1 H, *J* = 12.0 Hz, H-1′b), 4.50 (m, 4 H, H-6a, H-5′ or H-5 and 2 H-6′), 4.35 (dd, 1 H, *J* = 12.4, 3.2 Hz, H-6b), 1.72 (d, 3 H, *J* = 6.8 Hz, C*H*$_3$CH=CHCO).

^{13}C NMR ($CDCl_3$): δ = 17.82 (*C*H$_3$CH=CHCO), 62.28, 63.16, 64.78 (C-6, C-1′ and C-6′), 68.94, 69.12, 70.03, 71.25 (C-2, C-3, C-4 and C-5), 76.06, 77.38 (C-3′ and C-4′), 79.04 (C-5′), 90.80 (C-1), 104.58 (C-2′), 121.84, 128.21–133.55 (Ar and *C*H=*C*H), 164.99, 165.25, 165.42, 165.68, 165.76, 166.94 (8 CO).

Anal. Calcd for $C_{65}H_{54}O_{19}$ (1139.11): C, 68.54; H, 4.78. Found: C, 68.34; H, 4.94.

6′-*O*-(Crotonyl)-2,3,4,6,1′,3′,4′-hepta-*O*-(tri-*O*-methylgalloyl)-sucrose (13)

The reaction of **7** (0.17 g, 0.1 mmol) with crotonic anhydride (0.017 mL, 0.1 mmol) was carried out according to the general procedure during 30 min. Chromatographic purification (silica gel, EtOAc–hexane, 2:1) afforded 0.14 g (81%) of **13**; $[\alpha]_D$ +18.1 (*c* = 0.3, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 7.41–7.01 (7 s, 14 H, Ar), 6.91 (dq, 1 H, *J* = 15.6, 6.8 Hz, H-β), 6.23 (d, 1 H, *J* = 3.6 Hz, H-1), 5.98 (t, 1 H, *J* = 10.0 Hz, H-3), 5.94 (d, 1 H, *J* = 4.8 Hz, H-3′), 5.80–5.69 (m, 3 H, H-4, H-4′ and H-α), 5.19 (dd, 1 H, *J* = 10.4, 3.6 Hz, H-2), 4.78–4.52 (m, 7 H, H-5, H-6a, 2 H-1′, H-5′ and 2 H-6′), 4.22 (dd, 1 H, *J* = 13.8, 3.4 Hz, H-6b), 3.93–3.68 (10 s, 63 H, 21 CH_3O), 1.77 (d, 3 H, *J* = 13.6, C*H*$_3$CH=CHCO).

^{13}C NMR ($CDCl_3$): δ = 18.64 (*C*H$_3$CH=CHCO), 56.50–56.95 (*C*H$_3$OAr), 61.51 (*C*H$_3$OAr), 63.23, 64.02, 65.34 (C-6, C-1′ and C-6′), 69.85, 70.02, 71.18, 72.75 (C-2, C-3, C-4 and C-5), 77.10, 78.01 (C-3′ and C-4′), 80.71 (C-5′), 91.65 (C-1),106.14 (C-2′), 107.54–153.75 (Ar), 165.43, 165.63, 165.79, 165.87, 165.96, 166.27, 166.30, 166.43 (8 CO).

Anal. Calcd for $C_{86}H_{96}O_{40}$ (1769.70): C, 58.37; H, 5.47. Found: C, 58.03; H, 5.71.

Copolymerization of 9

Copolymerizations of compound **9** with styrene or methyl methacrylate were carried out in anhyd toluene (0.02 M) in the presence of AIBN as radical initiator (1 mol% by weight with respect to the monomer mixtures). All solutions were flushed with argon in order to remove oxygen. The reactions were kept at 70 °C for 24 h. Then, the solutions were cooled to r.t. and the product precipitated by dropwise addition into excess of cold (0 °C) EtOH. The white solids were filtered and washed several times with EtOH. The polymers were purified by repeated dissolution in toluene and reprecipitation in cold EtOH and subsequently dried in vacuum at 60 °C. Polymerization yields and compositions of the copolymers are reported in the Table.

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