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# Regioselective Copolymerization of Acryl Sucrose Monomers

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*Received June 21, 2004*

**Abstract:** 1′,2,3,3′,4,4′,6-Hepta-*O*-benzyl-sucrose has been prepared and selectively 6′-O-esterified with small α,β-unsaturated acid derivatives. New chiral copolymers containing sucrose have been synthesized by radical polymerization, and some of their physical properties have been determined.

Sugars are an important resource for the development of new materials such as water-soluble and/or biocompatible polymers owing to their low price.[1,2] Sucrose, as a cheap bulk product, could play an important role for this purpose. Some possible applications for sucrose-based polymers are drug delivery systems, dental medicine, bioimplants, contact lenses, and tissue engineering.[3,4] For these and other applications, they have the advantage of being potentially biodegradable.

In 1946, Haworth and co-workers[5] first reported the preparation of polymerization products from substituted carbohydrates containing acrylate or methacrylate groups. Since then, there has been extensive interest in the synthesis and polymerization of monofunctionalized carbohydrate monomers. In 1991 Dordick et al. reported a poly(sucrose acrylate) and poly(sucrose adipamide) synthesis with the help of an enzyme (Proleather, an alkaline protease from a *Bacillus* sp.).[6] Deffieux et al. have prepared monomethacryloyl sucrose esters by two different routes, in aqueous media and in organic solvent,[7] as well as several ethylenic acetals of sucrose[8] and have examined their homo- and copolymerization with styrene. Akashi et al. have synthesized methacryloyl and acryloyl-type glucose-containing vinyl monomers and have shown that it is possible to produce them on an industrial scale. They also prepared hydrogels from them and showed some practical applications for these products.[9] The synthesis of a water-soluble monomer, derived from D-gluconolactone, is described.[10] The homopolymerization of the vinylsugar has been conducted in both aqueous and organic media using free-radical initiators, forming high-molar-mass water-soluble polymers. Sugar-based hydrogels, obtained by nonselective modification of sucrose with the introduction of vinyl groups,[11] and the synthesis of a monomeric methacrylate ester of D-galactopyranose and its copolymerization with ethyl acrylate have also been described.[12]

Because sucrose has eight chemically active hydroxyl groups, regioselective derivatization is important in the selective synthesis of sucrose-containing linear polymers.[13,14] The route to selective derivatization of the 6′-position of the sucrose has been developed in our laboratory.[15,16] It allowed us to obtain the fully protected sucrose with only the 6′-hydroxyl unprotected, and we have prepared unsaturated sucrose esters from this intermediate. This monomer could be converted into pure linear polymers, avoiding the formation of mixtures of di- and higher substituted unsaturated esters, which results in cross-linked polymers.[17]

Here, the synthesis of these sugar monomers is presented. A study on the copolymerization of these sugar monomers with styrene and methyl methacrylate, as well as some physical properties of the resulting polymeric materials, is also reported.

The first step to our target consisted of a regioselective silylation of the 6′-hydroxyl group (Scheme 1) of the sucrose using *tert*-butyldiphenylchlorosilane (TBDPSCl) in dry pyridine at room temperature according to the methods described earlier.[18] By closely following the reaction by TLC and stopping the reaction when di-TBDPS first appeared, the yield was optimized up to 85%.

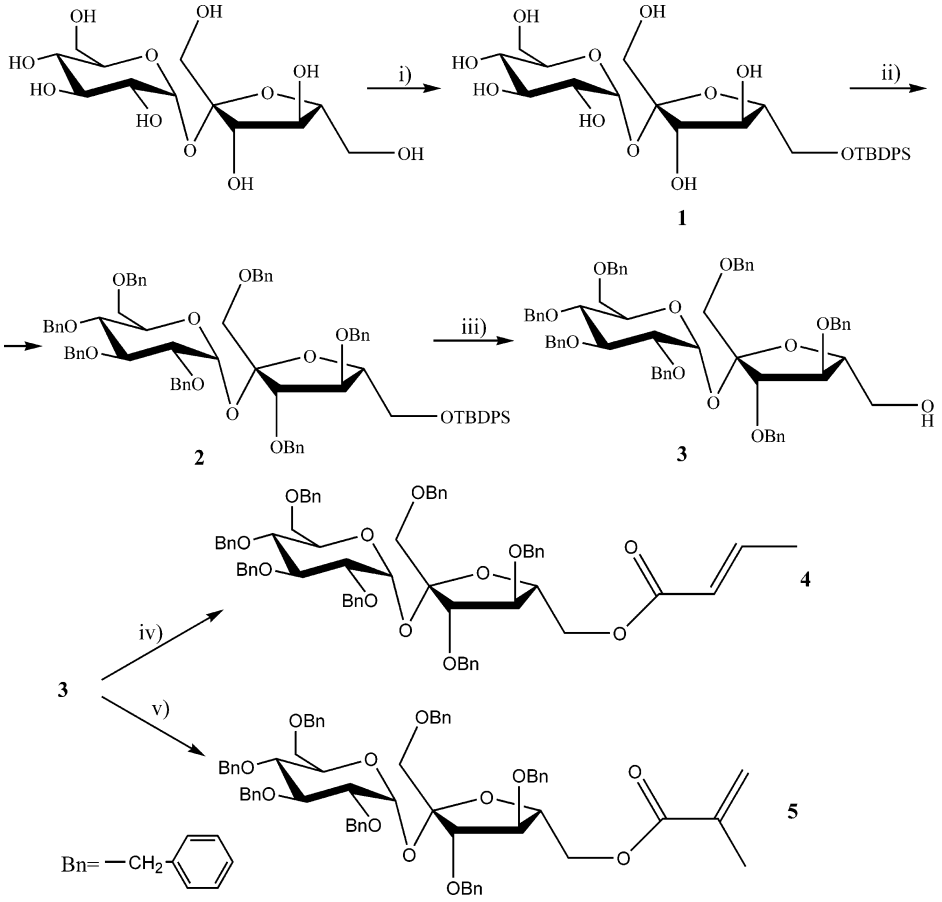
The monosilylated sucrose **1** was benzylated with benzyl bromide in DMF in the presence of NaH and $Bu_4N^+I^-$ as a catalyst, leading to the compound **2**.[19] Because of a slight instability of the TBDPS protecting group under the basic reaction conditions, we have always obtained the octabenzylated sucrose as a byproduct in yields of about 20% for this step. The yield was optimized by controlling the reaction temperature; the reagents were mixed at 0 °C, and the mixture then was allowed to warm to room temperature (below 30 °C), (Scheme 1).

Selective deprotection of the silyl group, with TBAF in THF at room temperature,[20] led to compound **3** in 85% yield after column chromatography (Scheme 1).

(1) Descotes, G. In *Carbohydrates as Organic Raw Materials*; Lichtenthaler, F. W., Ed.; VCH: Weinheim, New York, 1991.
(2) Dordick, J. S.; Linhardt, R. J.; Renthwish, D. *Chemtech* **1994**, 33.
(3) Pachence, J. M.; Kohn, J. In *Principles of Tissue Engineering;* Lanza, R. P., Langer, R., Vacanti, J., Eds.; Academic Press: New York, 2000.
(4) Lanza, R.; Langer, R.; Chick, W.; Academic Press/R.G. Landes Company: New York, 1997; Chapter 19, pp 273−285.
(5) Haworth, W. N., Gregory, H., Wiggins, K. F. *J. Chem. Soc.* **1946**, 488.
(6) Patil, D. R.; Dordick, J. S.; Rethwisch, D. *Macromolecules* **1991**, *24*, 3462.
(7) Jhurry, D.; Deffieux, A.; Fontanille, M.; Betremieux, I.; Mentech, J.; Descotes, G. *Makromol. Chem.* **1992**, *193*, 2297.
(8) Fanton, E.; Fayet, C.; Gelas, J.; Jhurry, D.; Deffieux, A.; Fontanille, M. *Carbohydr. Res.* **1992**, *226*, 337.
(9) Akashi, M.; Sakamoto, N. *Kagaku Kogyo* **1994**, *45* (6), 507−515.
(10) Narain, N.; Jhurry, D.; Wulff, G. *Eur. Polym. J.* **2002**, *38*, 273−280.
(11) Ferreira, L.; Vidal, M.M.; Geraldes, C. F. G. C.; Gil, M. H. *Carbohydr. Polym.* **2000**, *41*, 15.
(12) Carneiro, M. J.; Fernandes, A.; Figueiredo, C. M.; Fortes, A. G.; Freitas, A. M. *Carbohydr. Polym.* **2001**, *45*, 135.
(13) Fanton, E. M.; Fayet, C.; Gelas, J.; Deffieux, A.; Fontanille, M.; Jhurry, D. *Carbohydr. Res.* **1993**, *240*, 143−152.
(14) Potier, P.; Bouchou, A.; Descotes, G.; Queneau, Y. *Tetrahedron Lett.* **2000,** *41*, 3597.
(15) Barros, M. T.; Siñeriz, F. *Synthesis* **2002**, *10*, 1407−1411.
(16) Barros, M. T., Maycock, C. D., Siñeriz, F., Thomassigny, C. *Tetrahedron* **2000**, *56*, 6511.
(17) Chen, J.; Park, K. *Carbohydr. Polym.* **2000**, *41*, 259.
(18) Karl, H., Lee, C. K., Khan, R. *Carbohydr. Res.* **1982**, *101*, 31−38.
(19) Jarosz, S.; Kosciolowska, I. Poland 177,187, 1999.

10.1021/jo048957y CCC: $27.50 
Published on Web 10/06/2004

**SCHEME 1. Synthesis of Acryl Sucrose Monomers**[a]




[a] Reaction conditions: (i) TBDPSCl, py, 4-DMAP, rt, 85%; (ii) BnBr/NaH, DMF, $Bu_4N^+I^-$, rt, 80%; (iii) TBAF, THF, rt, 85%; (iv) $(CH_3CH{=}CHCO)_2O$, $CH_2Cl_2$, $Et_3N$, 4-DMAP, rt, 81%; (v) $(CH_2{=}C(CH_3)CO)_2O$, $CH_2Cl_2$, $Et_3N$, 4-DMAP, rt, 73%.

**TABLE 1. Copolymerization of 4 with Styrene or Methyl Methacrylate in the Presence of Radical Initiator AIBN in Mild Conditions (Toluene, 70 °C) and in and Autoclave (Toluene, 150 °C)**

| alkene | $[\mathbf{4}]_0$[a]/$[C]_0$ | [4][b]/[C] | reaction time [h] | yield (%) | $M_w$[c] | $M_w/M_n$ | $[\alpha]_D$ | $T_g$[d] [°C] |
|---|---|---|---|---|---|---|---|---|
| styrene | 0.1 | 0.016 | 96 | 12.9 | 10777 | 1.4 | +3.40 (*c* 1.00, $CHCl_3$) | 87.42 |
| styrene (autoclave) | 1.0 | 0.151 | 48 | 9.8 | 2917 | 1.2 | +8.57 (*c* 0.42, $CHCl_3$) | 74.93 |
| methyl methacrylate | 0.1 | 0.0015 | 96 | 23.3 | 26211 | 1.4 | +5.53 (*c* 1.00, $CHCl_3$) | 116.72 |

[a] Initial mole ratio of monomers. [b] Mole ratio of comonomer units in copolymer, determined by $^1$H NMR. [c] Determined by SEC with $CHCl_3$ as solvent using polystyrene standards. [d] Determined by DSC.

Esterifications of the free 6′-hydroxyl of **3** were carried out by treating it in a mixture of dichloromethane and triethylamine, at room temperature, with the appropriate anhydride to afford the expected compounds **4** and **5** in good yields (Scheme 1).

The $^1$H NMR spectra of these compounds exhibit two signals that have been attributed to the double bond: for crotonate **4** a mutiplet at 6.90 ppm and a doublet at 5.80 ppm and for methacrylate **5** a singlet at 6.15 ppm and a doublet at 5.60 ppm. We assigned the allylic methyl groups of the molecules at 1.70 ppm for **4** and 1.95 ppm for **5**.

The copolymerization of monomers **4** and **5** with styrene and methyl methacrylate has been examined in the presence of AIBN as free-radical initiator in toluene at 70 °C under normal pressure (mild conditions) and at 150 °C under pressure in an autoclave, followed by precipitation in cold ethanol. A study of the effect of the reaction conditions, the monomer structure, and the initial quantity of the comonomers on the sugar incorporation in the final copolymers has been carried out. As a result we obtained a number of copolymers with diverse contents of protected sucrose, with different chain length, reported by the weight average molecular weight, $M_w$, polidispersity, $M_w/M_n$ (being $M_n$ the number average molecular weight), and different physical properties such as optical rotations, $[\alpha]_D$, and glass transition temperatures, $T_g$ (Tables 1 and 2).

Copolymer composition has been determined by $^1$H NMR. When the comonomer is methyl methacrylate, the structures have been verified by comparing the peak areas of the methylene, methyl (0.8−2.2 ppm), and methoxy (3.6 ppm) protons of the polymer chain with the 14 sucrose unit protons.

(20) Chênevert, R.; Caron, D. *Tetrahedron: Asymmetry* **2002**, *13*, 339−342.

**TABLE 2. Copolymerization of 5 with Styrene or Methyl Methacrylate in the Presence of Radical Initiator AIBN in Mild Conditions (Toluene, 70 °C) and in an Autoclave (Toluene, 150 °C)**

| alkene | $[\mathbf{5}]_0{}^a/[C]_0$ | $[\mathbf{5}]^b/[C]$ | reaction time [h] | yield (%) | $M_w{}^c$ | $M_w/M_n$ | $[\alpha]_D$ | $T_g{}^d$ [°C] |
|---|---|---|---|---|---|---|---|---|
| styrene | 1.0 | 0.160 | 120 | 70.70 | 6856 | 1.3 | +24.86 (*c* 1.00, $CHCl_3$) | 90.88 |
| styrene | 1.0 | 0.100 | 96 | 36.02 | 30968 | 1.9 | +28.80 (*c* 1.00, $CHCl_3$) | 56.70 |
| styrene (autoclave) | 1.0 | 0.263 | 48 | 64.27 | 12575 | 1.5 | +27.17 (*c* 1.01, $CHCl_3$) | 94.84 |
| styrene (autoclave) | 1.0 | 0.083 | 24 | 44.90 | 6649 | 1.3 | +32.52 (*c* 1.07, $CHCl_3$) | 53.27 |
| methyl methacrylate | 1.0 | 0.435 | 168 | 41.05 | 14829 | 1.4 | +26.80 (*c* 1.00, $CHCl_3$) | 115.62 |
| methyl methacrylate | 1.0 | 0.124 | 120 | 55.90 | 18382 | 1.8 | +27.85 (*c* 0.79, $CHCl_3$) | 64.90 |
| methyl methacrylate (autoclave) | 1.0 | 0.526 | 48 | 79.02 | 12149 | 1.4 | +20.96 (*c* 0.94, $CHCl_3$) | 115.50 |
| methyl methacrylate (autoclave) | 1.0 | 0.228 | 24 | 59.72 | 17280 | 1.6 | +41.54 (*c* 0.78, $CHCl_3$) | 97.60 |

[a] Initial mole ratio of monomers. [b] Mole ratio of comonomer units in copolymer, determined by $^1$H NMR. [c] Determined by SEC with $CHCl_3$ as solvent using polystyrene standards. [d] Determined by DSC.

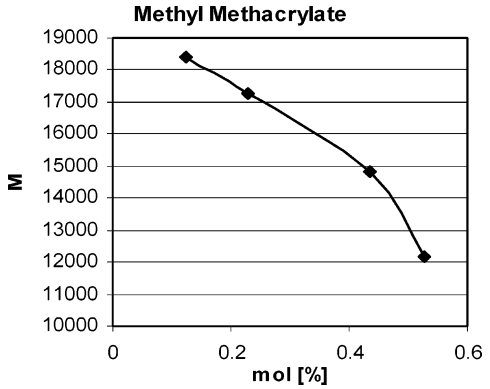



**FIGURE 1.** Molecular weights of the copolymers versus mole percent of incorporation of 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-*O*-methacryloyl-sucrose (**5**) in poly(**5**-*co*-methyl methacrylate).

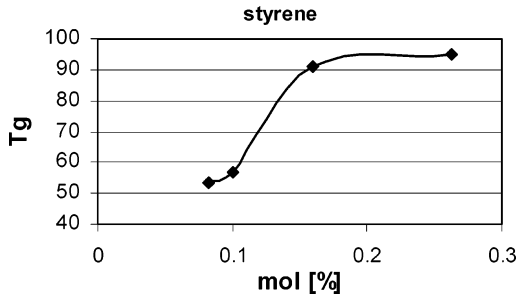



**FIGURE 2.** Glass transition temperatures versus mole percent of incorporation of 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-*O*-methacryloyl-sucrose (**5**) in poly(**5**-*co*-styrene).

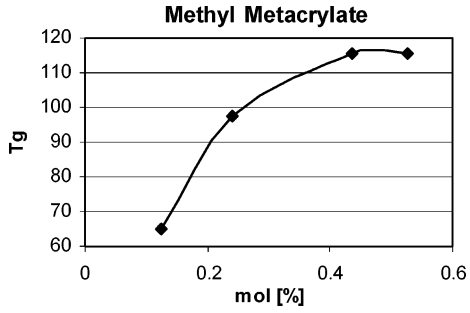



**FIGURE 3.** Glass transition temperatures versus mole percent of incorporation of 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-*O*-methacryloyl-sucrose (**5**) in poly(**5**-*co*-methyl methacrylate).

The analysis of the results presented in Table 1 showed that using the same initial molar composition of the monomers and reaction conditions, we got 10 times lower incorporation of the sugar in the polymer in the case of using methyl methacrylate than with styrene. Also, with an excess of methyl methacrylate a very low incorporation of sugar was obtained at normal pressure. Therefore, all subsequent experiments with sucrose monomer **5** were carried out with equimolar initial ratio of comonomers.

Comparing the behavior of sucrose derivatives, the compound with a terminal double bond (**5**), which is expected to be more reactive, readily gave copolymers with a considerable molecular weight (up to 30 000), both under mild conditions and in the autoclave, whereas the crotonoyl sucrose (**4**) failed to react under mild conditions to give copolymers with significant sucrose content.

The majority of the results obtained for the copolymerization of sucrose derivative **5** show that we got polymers with a lower incorporation of sucrose than alkene, as it was expected. Nevertheless, two interesting copolymers were achieved with methyl methacrylate, in mild conditions (168 h) and under pressure (48 h), with molar ratios [V]/[C] = 0.435 and 0.526, respectively, corresponding to the highest sucrose derivative content obtained. The highest chemical yield value (79.02%) was observed for the copolymer **5**/methyl methacrylate, with the best monomer **5** incorporation.

Concerning the effect of the pressure on both reaction systems, **5**/styrene and **5**/methyl methacrylate, it is not possible to establish any correlation between this parameter and the results obtained.

As expected, optical rotations were lower in the polymers with larger incorporation of the nonoptically active comonomer and were generally higher for the copolymers with methacrylic moiety.

Data obtained by size exclusion chromatography (SEC) analysis revealed monomodal molecular weight distributions. Copolymer average molecular weights ($M_w$), estimated by the same method, were in a range of values similar to those of similar copolymers reported in the literature (10−20 000)[2]. In general, the molecular weights of the copolymers were decreasing for the polymers with larger incorporation of the sugar comonomer (Figure 1), which is less reactive and also provides more possibilities for chain transfer reactions in the reaction mixture. All of the values of polydispersity obtained are very low, varying between 1.2 and 1.9, which means that the copolymers are very homogeneous.

All copolymers synthesized are amorphous, bearing only glass transition temperature. Glass transition temperatures were increasing exponentially with the mole percent of sugar incorporation for the copolymers with methacrylic moiety, both with styrene and methyl methacrylate (Figures 2 and 3), probably as a result of the

restrained movements of the polymer molecule with more bulky substituents.

In summary, 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-sucrose has been prepared and selectively 6′-O-esterified with small α,β-unsaturated acid derivatives. New chiral copolymers containing sucrose have been synthesized by radical polymerization, and some of their physical properties were determined.

## Experimental Section

Reagents and solvents were purified before use.[21] All reactions were carried out under a positive pressure of dry argon. Optical rotations were measured at 20 °C on an AA-1000 polarmeter (0.5 dm cell). NMR spectra were recorded at 400 MHz in $CDCl_3$ with chemical shift values ($\delta$) in ppm downfield from TMS. Average molecular weights were determined using a size exclusion chromatography (SEC) apparatus, including a solvent delivery system composed of a pump, injector, and refractive index detector. The operation temperature was 30 °C, chloroform was used as eluent with a series of three columns, $10^3$, $10^4$, and $10^5$ Å, and the calibration was performed with monodisperse polystyrene standards. Glass transition temperatures were measured at the second heating cycle with a rate of 10 °C/min.

**6′-O-*tert*-Butyldiphenylsilyl-sucrose (1).**[18] A solution of sucrose (5.00 g) in dry pyridine (70 mL) was stirred with 4-(dimethylamino)pyridine (0.05 g) and 1.1 molar equiv of *tert*-butyldiphenylsilyl chloride (3.9 mL) at room temperature and monitored by TLC (ethyl acetate−acetone−water, 10:10:1). When the less polar 6,6′-di-OTBDPS-sucrose appeared ($R_f$ 0.49, 4−5 h), the reaction mixture was concentrated and purified by column chromatography (ethyl acetate to ethyl acetate−acetone−water, 100:100:1) to yield 7.208 g (85%) of **1**. $^1$H NMR ($CDCl_3$): $\delta$ 7.66(m, 4H), 7.41(m, 6H), 5.60(d, $J$ = 3.7 Hz, 1H), 5.52(t, $J$ = 5.7 Hz, 1H), 5.40(t, $J$ = 9.8 Hz, 1H), 5.39(d, $J$ = 5.6, 1H), 5.03(t, $J$ = 9.9 Hz, 1H), 4.80(dd, $J$ = 10.3, 3.7 Hz, 1H), 4.70(s, 1H), 4.17−3.93(m, 7H), 1.06(s, 9H). $[\alpha]^{20}_D$ +44°(*c* 1, methanol).

**1′,2,3,3′,4,4′,6-Hepta-*O*-benzyl-6′-*O*-*tert*-butyldiphenylsilyl-sucrose (2).**[19] 6′-O-*tert*-Butyldiphenylsilylsucrose (**1**) (0.5000 g, 0.862 mmol) was dissolved in 10 mL of DMF together with a catalytic amount (5 mg) of $(n\text{-Bu})_4N^+I^-$. The solution was cooled to 0 °C, and 0.463 g NaH (50% suspension in oil, 11.2 equiv) was added carefully. After 20 min 1.46 mL of benzyl bromide (14 equiv) was added drop by drop for 15 min. The ice bath was removed, and the reaction was monitored by TLC (hexanes−ethyl acetate, 5:1). When there was no more of the initial compound (4−5 h), the reaction mixture was poured into $H_2O$ (100 mL). The product was extracted 4 times with 40 mL of diethyl ether, and the collected organic layers were washed twice with 10 mL of $H_2O$, dried with $Na_2SO_4$, and concentrated. The residue was purified by column chromatography (eluent hexanes−ethyl acetate, 5:1) to yield 0.8345 g (80%) of **2**. $^1$H NMR ($CDCl_3$): $\delta$ 7.37−7.13(m, 45H), 5.72(d, $J$ = 3.7 Hz, 1H), 4.83(d, $J$ = 11.0 Hz, 1H), 4.79(d, $J$ = 11.0 Hz, 1H), 4.72−4.33(m, 14H), 4.18(d, $J$ = 12.0 Hz, 1H), 4.11(dd, $J$ = 11.2, 5.5 Hz, 1H), 4.09−4.05(m, 1H), 3.93(t, $J$ = 9.2 Hz, 1H), 3.75−3.62(m, 3H), 3.55−3.47(m, 2H), 3.37(dd, $J$ = 10.1, 2.4 Hz, 1H), 1.25(s, 9H). $^{13}$C NMR ($CDCl_3$): $\delta$ 19.1, 26.8, 65.0, 68.4, 70.5, 71.2, 72.1, 72.4, 73.1, 73.3, 73.4, 74.7, 75.5, 77.5, 79.9, 81.3, 82.0, 82.7, 84.2, 89.8, 104.7, 127.5−139.1. $[\alpha]^{20}_D$ +30.9(*c* 0.9, $CHCl_3$).

**1′,2,3,3′,4,4′,6-Hepta-*O*-benzyl-sucrose (3).**[10] Compound **2** (500 mg, 0.413 mmol), dissolved in 10 mL of dry THF, was treated with tetrabutylammonium fluoride (0.496 mL, 0.496 mmol, 1 M solution in THF) at room temperature, and the reaction monitored by TLC (hexanes−ethyl acetate, 3:1). When no more of the starting material remained (4−5 h), the solvent was evaporated. The residue was dissolved in dichloromethane, washed twice with $H_2O$, dried, and concentrated. Purification by flash column chromatography (eluent hexanes−ethyl acetate, 3:1) yielded 0.3414 g (85%) of **3**. $^1$H NMR ($CDCl_3$): $\delta$ 7.37−7.13(m, 35H), 5.72(d, $J$ = 3.7 Hz, 1H), 4.83(d, $J$ = 11.0 Hz, 1H), 4.79(d, $J$ = 11.0 Hz, 1H), 4.72−4.33(m, 14H), 4.18(d, $J$ = 12.0 Hz, 1H), 4.11(dd, $J$ = 11.2, 5.5 Hz, 1H), 4.09−4.05(m, 1H), 3.93(t, $J$ = 9.2 Hz, 1H), 3.75−3.62(m, 3H), 3.55−3.47(m, 2H), 2.29(s, 1H). $^{13}$C NMR ($CDCl_3$): $\delta$ 68.5, 66.9, 68.6, 70.3, 72.3, 72.4, 73.2, 73.5, 73.6, 75.0, 75.7, 77.8, 79.6, 79.9, 81.9, 82.5, 83.9, 89.9, 104.6, 127.6−138.9. $[\alpha]^{20}_D$ +46.12(*c* 1.34, $CHCl_3$)

**1′,2,3,3′,4,4′,6-Hepta-*O*-benzyl-6′-*O*-crotonyl-sucrose (4) and 1′,2,3,3′,4,4′,6-Hepta-*O*-benzyl-6′-*O*-methacryloyl-sucrose (5).**[5] To a 0.1 M solution of **3** (500 mg, 0.514 mmol) in anhydrous $CH_2Cl_2$ were added $Et_3N$ (130 mg, 1.286 mmol) and a catalytic amount of 4-DMAP. The mixture was cooled to 0 °C, and then a 0.5 M solution of crotonic/methacrylic anhydride (1.2 equiv) in anhydrous $CH_2Cl_2$ was added. The reaction mixture was allowed to warm to room temperature. When no more starting material remained, more $CH_2Cl_2$ was added (5 × 15 mL per mmole of starting material) and washed with aqueous 1.0 N HCl (15 mL per mmole of starting material), saturated aqueous $NaHCO_3$, and distilled $H_2O$. The organic layer was dried ($Na_2SO_4$), and the solvent was evaporated. Purification by flash column chromatography (eluent hexanes−ethyl acetate, 5:1) yielded 0.4333 g (81%) of **4** and 0.3905 (73%) of **5**.

**Data for 4.** $^1$H NMR ($CDCl_3$): $\delta$ 7.37−7.13(m, 35H), 6.90(dq, $J$ = 15.6, 6.8, 1H), 5.80(d, $J$ = 15.6, 1H), 5.72(d, $J$ = 3.7 Hz, 1H), 4.83(d, $J$ = 11.0 Hz, 1H), 4.79(d, $J$ = 11.0 Hz, 1H), 4.72−4.33(m, 14H), 4.18(d, $J$ = 12.0 Hz, 1H), 4.11(dd, $J$ = 11.2, 5.5 Hz, 1H), 4.09−4.05(m, 1H), 3.93(t, $J$ = 9.2 Hz, 1H), 3.75−3.62(m, 3H), 3.55−3.47(m, 2H), 1.75 (s, 3H). $[\alpha]^{20}_D$ +48.12(*c* 1.33, $CHCl_3$). Anal. Calcd: C, 74.98; H, 6.58. Found: C, 74.74; H, 6.66.

**Data for 5.** $^1$H NMR ($CDCl_3$): $\delta$ 7.37−7.13(m, 35H), 6.15(d, $J$ = 3.6 Hz, 1H), 5.55(d, $J$ = 3.6 Hz, 1H), 5.72(d, $J$ = 3.7 Hz, 1H), 4.83(d, $J$ = 11.0 Hz, 1H), 4.79(d, $J$ = 11.0 Hz, 1H), 4.72−4.33(m, 14H), 4.18(d, $J$ = 12.0 Hz, 1H), 4.11(dd, $J$ = 11.2, 5.5 Hz, 1H), 4.09−4.05(m, 1H), 3.93(t, $J$ = 9.2 Hz, 1H), 3.75−3.62(m, 3H), 3.55−3.47(m, 2H), 2.00(s, 3H). $[\alpha]^{20}_D$ +46.88 (*c* 1.23, $CHCl_3$). Anal. Calcd: C, 74.98; H, 6.58. Found: C, 74.69; H, 6.88.

**General Procedure for Copolymerization under Mild Conditions.** Copolymerizations of compounds **4** and **5** with styrene or methyl methacrylate were carried out in anhydrous toluene solutions (0.1 M) in the presence of AIBN as radical initiator (1 wt % with respect to the monomer mixture). Dissolved oxygen was removed from the solutions by three freeze−thaw cycles on the vacuum pump. They were then heated at 85 °C until the polymerizations were complete, the solutions were then cooled to room temperature, and the product was precipitated in cold EtOH. The white solid was filtered and washed several times with cold EtOH. The polymers were purified by repeated dissolution in toluene and reprecipitation in cold EtOH and dried under vacuum. The yields and some physical properties of thus prepared polymers are shown in Tables 1 and 2.

**General Procedure for Copolymerization in an Autoclave.** The autoclave copolymerizations of compounds **4** and **5** with styrene or methyl methacrylate were carried out in anhydrous toluene solution (0.1 M) in the presence of AIBN as radical initiator (1 wt % with respect to the monomer mixture). The solutions were placed in an autoclave vessel and kept at 150 °C for 24 h. The solutions were then cooled to room temperature, and 0.05-mL samples were taken from the mixture and dropped into ethanol. If there was no precipitation, the mixture was heated for another 24 h. As soon as precipitation appeared, the reaction was stopped by precipitating the whole mixture in cold EtOH. The white solid was filtered and washed several times with cold EtOH. The polymers were purified by repeated dissolution in toluene and reprecipitation in cold EtOH and finally dried under vacuum.

**Acknowledgment.** This work has been supported by Fundação para a Ciência e a Tecnologia (SFRH/BPD/9474/2002 and POCTI/QUI/47973/2002).

JO048957Y

(21) *Purification of Laboratory Chemicals*, 2nd Ed.; Perrin, D. D., Armarego, W. L. F., Perrin, D. R., Eds.; Pergamon Press Ltd.: New York, 1980.