Carbohydrate Research, 240 (1993) 143–152
Elsevier Science Publishers B.V., Amsterdam

Synthesis of 4-*O*- and 6-*O*-monoacryloyl derivatives of sucrose by selective hydrolysis of 4,6-*O*-(1-ethoxy-2-propenylidene)sucrose. Polymerization and copolymerization with styrene

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(Received July 28th, 1992; accepted August 14th, 1992)

ABSTRACT

The synthesis of an ethylenic orthoester of sucrose by transorthoesterification of an acrylic reagent with sucrose is described. Mild hydrolysis of this orthoester gave sucrose selectively monosubstituted by an acryloyl group at either the 4-*O*- or the 6-*O*-position. These acrylates were homopolymerized and copolymerized with styrene, and the corresponding polymers were characterized.

INTRODUCTION

We have recently been engaged in a program devoted to the synthesis of polymers containing sucrose moieties and possessing properties such as water solubility or biodegradability. If, in general, suitable monomers for homo- and co-polymerization of sugars are now increasingly available, in the specific case of sucrose there is still a limited number of such derivatives[1]. In a previous paper[2] we described a convenient possible access to polymers from ethylenic acetals of sucrose.

The polymerization of acrylic and methacrylic derivatives is a well-known route to one of the most common, commercially available, family of polymers. Thus acryloyl and methacryloyl esters of sucrose are indeed good candidates for access to polymers with a polyvinylic backbone substituted by lateral sucrose moieties. Very few examples of this type of reaction involving sucrose can be found in the

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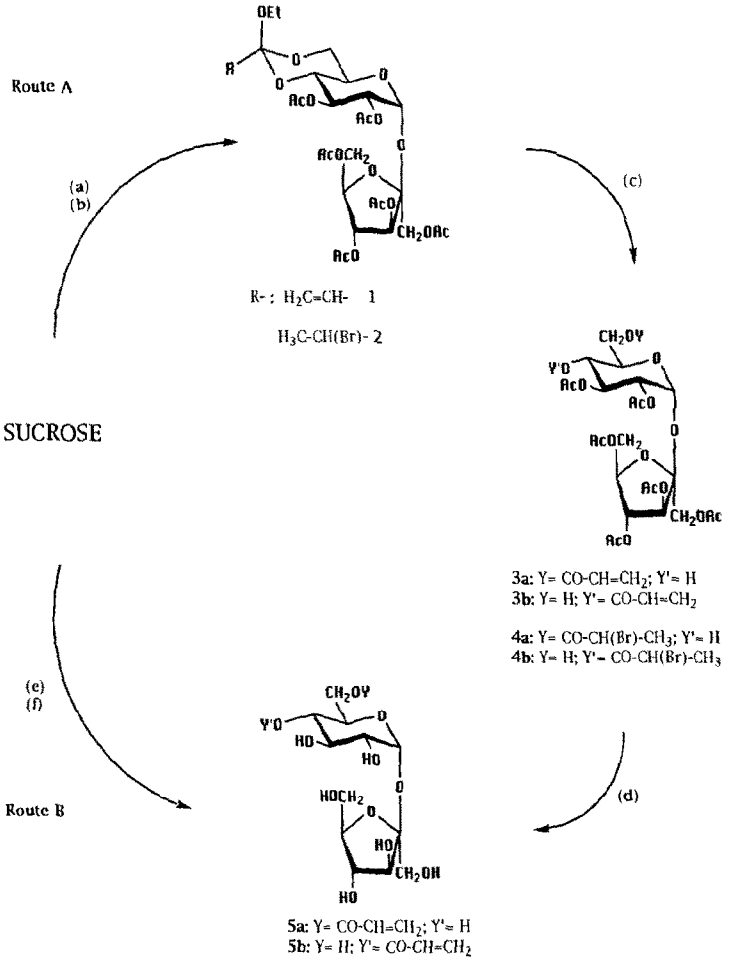
literature. A multistep procedure for the preparation of a monomer [1′,6,6′-tri-*O*-(2-methyl-2-propenoyl)sucrose] claimed to be potentially useful for future polymerizations has been recently described[3]. A highly reticulated (due to the multifunctionality of the starting monomer) polymethacrylate sucrose has been obtained[4]. On the other hand, the polymerization of 1′-*O*-acryloylsucrose, selectively prepared in moderate yield (28%) using an enzyme, has been reported[5]. The preparation of methacrylic esters of sucrose and their polymerization has also been thoroughly studied by Descotes et al.[6,7] and Fontanille et al.[7,8].

It is quite obvious that the key feature for any strategy should be the strict control of the monofunctionality of the monomer involved in the polymerization. It is well known that this is a major problem in carbohydrate chemistry[9] and specially so for sucrose[1a–1c]. In another program, we studied the selective orthoesterification of monosaccharides at nonanomeric positions[10] using either the transorthoesterification of orthoesters (which is a known reaction; see ref. 11 and references therein), or reaction under kinetic control using ketene acetals. The selective hydrolysis of such orthoesters is a known process[12] leading to monoesters. This study with ketene acetals was extended to sucrose[10], for which the transorthoesterification with triethyl orthoacetate and subsequent hydrolysis of the orthoester to a mixture of 6-*O*- and 4-*O*-acetyl sucrose has been published[13].

Finally, we thought that a strategy of choice for the synthesis of a polymerizable sucrosyl monomer could be the selective orthoesterification of sucrose, leading to an ethylenic orthoester, mild hydrolysis of which could give access to a mono- (or a mixture of mono-) acrylate(s).

RESULTS AND DISCUSSION

Transorthoesterification of sucrose using triethyl orthoacrylate leads to 4,6-*O*-(1-ethoxy-2-propenylidene)sucrose (**1**, Scheme 1). The reagent has been obtained according to Stetter and Uerdingen[14] by addition of bromine to triethylorthopropionate, followed by dehydrohalogenation in basic medium. Then, transorthoesterification of sucrose was carried out in anhyd *N*,*N*-dimethylformamide, under mild acidic conditions, at room temperature, in the presence of pyridinium *p*-toluenesulfonate. After classical acetylation of the crude reactional mixture, and column chromatography, **1** was obtained as a pure compound in 20% yield (which has not been optimized). Unreacted sucrose octaacetate was also collected, and partial degradation of **1** on silica gel has been noted. This reaction is regioselective as only the 4,6-*O*-monoorthoester, which has been identified on the basis of its NMR spectral data, is obtained under these conditions. The ^{1}H NMR spectrum shows, in particular, a multiplet at 1.2 ppm and a quartet at 3.4 ppm corresponding to the ethoxyl group, and a signal at 5.4 ppm due to the vinylic protons. The structure was confirmed by the ^{13}C NMR spectrum that shows the presence of the carbon atom of the orthoester function with a signal at 109.8 ppm, which is in accord with previous observations[10,11] for six-membered orthoesters.



(a) R-C(OEt)$_3$; DMF; Py$^+$H,TsO$^-$. (b) Ac_2O, Pyridine. (c) AcOH/H_2O. (d) MeONa, MeOH (starting from 3). (e) H_2C=CH-C(OEt)$_3$; DMF; Py$^+$H,TsO$^-$. (f) H_2O; Py$^+$H,TsO$^-$ or H_2O, silica gel.

Scheme 1.

Selective acidic hydrolysis of **1** with 20% aq acetic acid affords the corresponding monoester (50% yield after chromatographic purification), which actually consists of a mixture of the two possible positional isomers, the 6-*O*- and 4-*O*-(2-propenoyl) sucrose **3a** and **3b** (Scheme 1). Both structures were confirmed by (*i*) the presence in the ^{1}H NMR spectrum of a signal at 5.8–6.4 ppm due to the acrylate group protons, (*ii*) by the disappearance in the ^{13}C NMR spectrum of the signal at 109.8 ppm observed for compound **1**, and by the presence of a new singlet at 106.6 ppm corresponding to the carbon atom of an ester. The presence of 4-*O*- and 6-*O*-acryloyl sucrose after hydrolysis of **1** was confirmed by the examination of

the ^{1}H NMR spectrum of compound **6**, 4 (or 6)-*O*-acetyl-1′,2,3,3′,4′,6′-hexa-*O*-deuteroacetyl-6(or 4)-*O*-acryloylsucrose obtained by acetylation of **3a** and **3b** with deuteroacetic anhydride. The signals due to the methyl group of the acetyl residues may be observed at 2.08 ppm (4-*O*-acetyl) and 2.03 ppm (6-*O*-acetyl), with the ratio of 4-*O*-ester : 6-*O*-ester approximately 25 : 75.

As the corresponding bromoesters **4a** and **4b** were also interesting starting materials for polycondensations, we extended our synthesis to the preparation of hexa-*O*-acetyl-4,6-*O*-(2-bromo-1-ethoxypropylidene)sucrose (**2**), which was carried out from sucrose under the same conditions with triethyl 2-bromoorthopropionate. Compound **2** was obtained in a 40% yield, and its selective hydrolysis led to a mixture of 4-*O*- and 6-*O*-monoesters **4** in 50% yield (Scheme 1).

Thus the regioselectivity of the first step, followed by selective hydrolysis, results in the formation of a monofunctional sucrose derivative, which was our objective, while the syntheses of sucrose esters described in the literature generally lead to mixtures of mono-, di-, and tri-esters.

In order to scale up our procedure for industrial purposes, some modifications were carried out. First, a one-pot reaction is possible to reach compound **5** from a direct reaction of sucrose with triethyl orthoacrylate combined with the hydrolysis of the mixture (Scheme 1, Route B), carried out either by adding water and an additional amount of pyridinium *p*-toluenesulfonate to the reactional mixture, or by stirring the residue (after evaporation of *N*,*N*-dimethylformamide) with water and silica gel. After evaporation of the solvents, column chromatography directly gave **5** in 25% yield from sucrose. Before purification, proportions of sucrose and monoacrylates in the crude residue were determined by HPLC in the ratio of sucrose : monoacrylates 75 : 25.

It should be noted that for large-scale polymerizations it is possible to avoid this purification step and to directly react crude mixtures of sucrose and acrylates only after washing with 1 : 1 acetone–dichloromethane.

The homopolymerization of monomers **3** and **5**, and their copolymerization with styrene, have been examined in the presence of free-radical initiators. In the case of **3**, which contains blocked hydroxyl groups, homopolymerization experiments were carried out in toluene using azobis(isobutyronitrile) (AIBN) as initiator, while the homopolymerization of **5** was performed in aqueous medium in the presence of potassium persulfate. The experimental conditions and results are given in Table I. As can be seen, the homopolymerization of **3** leads only to low molar mass products, whereas substantially higher molar mass hydrosoluble polymers were obtained both with pure **5** and with **5** in the presence of remaining sucrose, suggesting that free hydroxyl groups of the latter do not act as the transfer agent. In dilute solutions (0.64 M) soluble poly-**5** having molar masses in the range of 10^6 were obtained. However, when **5** was polymerized in concentrated aqueous solutions (1.7 M), crosslinked hydrogels were formed. Similar results have been previously reported concerning *N*-acryloyl and *N*-methacryloyl derivatives of 1-amino-1-deoxy-D-glucitol[15] and 6-*O*-methacryloyl-D-galactose[16]. The exact mecha-

TABLE I

Homopolymerization of **3** and **5** in the presence of radical initiators

Sucrose monomer	Concn (mol l^{-1})	Solvent	Initiator	Yield (%)	M_n
3		Toluene	AIBN	65	4000 [a]
5	1.7	H_2O	$K_2S_2O_8$/TMEDA	– [b]	– [b]
	0.64	H_2O	$K_2S_2O_8$/TMEDA	50	$>10^6$ [c]

[a] Determined by SEC with THF as eluent using polystyrene as standards. [b] Formation of crosslinked polymer. [c] Determined by SEC with H_2O as eluent using poly(ethyleneglycol)s as standards.

nism of crosslinking is not known; the authors suggested that condensation reactions between hydroxyl groups might occur, thereby leading to intramolecular ether linkages. Another possible crosslinking reaction might involve intramolecular condensation between sucrose hydroxyl groups and carboxyl groups resulting from a partial deesterification of the sucrose acrylate. As indicated before, such processes are limited at low monomer concentrations, thus leading to a completely soluble polymers which were further studied. Before characterization of poly-**5**, residual sucrose was eliminated from the reaction mixture by dialysis. The IR and ^{1}H NMR spectra of the homopolymers are consistent with their expected structures. DSC thermograms do not reveal any transition in the range 25 to 250°C.

The copolymerization of **3** with styrene (S) was performed in toluene at 70°C, while copolymerization experiments involving **5** were carried out in a polar solvent such as *N*,*N*-dimethylformamide in order to simultaneously dissolve both comonomers and sucrose. Results are collected in Table II. Copolymer compositions were calculated from ^{1}H NMR spectra, either directly [poly(**3**-co-S)] or after acetylation [poly(**5**-co-S)], using the peak areas of styrene aromatic protons and acetate protons of sucrose units. The molar percentage of comonomers in the

TABLE II

Copolymerization of **3** and **5** with styrene (S) in the presence of a radical initiator (Solvent, DMF; temperature, 70°C; initiator, AIBN)

Monomer	$\frac{[M_0]}{[S_0]}$ [a]	$\frac{[M]}{[S]}$ [b]	Yield (%)	M_n [c]	Solubility of the copolymers		T_g	
					DMF, Me_2SO	H_2O	Unblocked	Blocked
3	0.33 [d]	0.08	35	18500	S [e]	X [e]		
5	0.22	0.3	25	21000	S	X	125	86
	1.0	1.7	59	22000	S	S	127	92
	3.0	1.86	52	16000	S	S	–	–

[a] Initial molar ratio of monomers. [b] Molar ratio of comonomer units in copolymer, determined by ^{1}H NMR after acetylation of OH groups. [c] Determined by SEC with THF as eluent using polystyrene as standards. [d] Solvent, toluene. [e] S, soluble, X, insoluble.

copolymers was found to be almost the same as that in the initial feed. In a previous communication[7], we reported the reactivity ratios in the copolymerization of 6-*O*-methacryloyl sucrose (MMAS) with styrene as $r_{MMAS} = 2.3$ and $r_S = 1.45$. In the present case, calculated values are as follows: $r_S = 1.90$ and $r_S = 0.95$. These values show the tendency for formation of blocks in copolymers. The molar mass of the copolymers have been estimated by SEC using polystyrene as standard. These were lower than that of the homopolymers, indicating a limiting effect of styrene on molar masses. Copolymers based on **3** and styrene were soluble in classical organic solvents such as toluene, dichloromethane, tetrahydrofuran, and acetone. However, as shown by the solubility characteristics given in Table II, copolymers derived from **5** and styrene were only soluble in polar solvents like *N*,*N*-dimethylformamide or dimethyl sulfoxide. Those having a high content of **5** (from 50%) were, furthermore, water soluble.

The influence of the hydroxyl groups of the sucrose moiety on the thermomechanical properties was assessed by comparing the glass transition temperatures of both blocked and unblocked copolymers (see Table II). The same effect as that previously reported[2,7] is observed. Copolymers having blocked hydroxyl groups have nearly the same T_g as polystyrene. On the contrary, T_g values of copolymers bearing free hydroxyl groups increased rapidly as the content of the sucrose monomer became higher due to an increase in the intermolecular forces.

EXPERIMENTAL

General methods.—Styrene was purified by distillation under reduced pressure over CaH_2. *N*,*N*-Dimethylformamide was distilled under reduced pressure over $MgSO_4$. Azobis(isobutyronitrile) and potassium persulfate were obtained commercially and used without further purification. Evaporations were performed under diminished pressure. Melting points were determined on a Büchi apparatus. Optical rotations were measured on a Perkin–Elmer 141 polarimeter in 1-dm tubes. Column chromatography was performed with Silica Gel 60 (E. Merck 70–230 mesh), and flash column chromatography with Silica Gel (Amicon 35–70 μm); TLC was carried out on precoated plates (E. Merck 5724), with detection by charring with H_2SO_4. ^1H NMR spectra (60 or 300 MHz) were recorded on a Varian T-60 spectrometer or on a Bruker MLS 300 spectrometer. Chemical shift data are given in δ-units (ppm) measured downfield from internal Me_4Si, and spin–spin coupling data are in Hz. ^{13}C NMR spectra were recorded on a JEOL FX 60 spectrometer. IR spectra were recorded on a Nicolet 320 FT spectrometer. HPLC analyses were performed on a Knauer chromatograph with an amino-derivatized silica gel column (Nucleosil-NH_2 5 μm, 4.6 × 250 mm) and a refractometric detector. A mixture of 3:1 acetonitrile–water was used as eluent. Size-exclusion chromatography (SEC) was performed on a Varian apparatus. In the case of homopolymers, a TSK 3000PW column calibrated with polyethyleneglycols was used, and, in the case of copolymers, 5TSK columns calibrated with polystyrene

standards were used. Glass transition temperatures were measured on a Metler TA 3000 apparatus at the second heating cycle at a rate of 10°C/min. Elemental analyses for C, H, Br, and O were carried out by the Service Central d'Analyses du C.N.R.S. in Lyon, France.

Preparation of triethyl orthoacrylate.—The preparation was carried out in two steps according to the method of Stetter and Uerdingen[14]. Triethyl 2-bromoorthopropionate was obtained in 58% yield, and triethyl orthoacrylate in 78% yield.

Typical run for synthesis of 4,6-O-orthoesters of sucrose (**1**) *and* (**2**).—To a suspension of sucrose in anhyd *N,N*-dimethylformamide stirred at room temperature, were added the reagent (respectively triethyl orthoacrylate or triethyl 2-bromoorthopropionate, 1.5 mol equiv with respect to sucrose) and a catalytic amount of pyridinium *p*-toluenesulfonate. The reaction was monitored by TLC (5:3:2 butanol–EtOH–water). After 20 h, the solution was neutralized with Na_2CO_3, filtered, and the solvent was evaporated under reduced pressure. The crude amorphous material was dissolved in anhyd pyridine, and acetic anhydride was added at 0°C to the stirred solution. After 24 h, the solution was poured onto ice–water, mixed with Na_2CO_3, and the mixture was extracted with CH_2Cl_2. The extracts were washed with a sat aq $NaHCO_3$ and dried (Na_2SO_4). The solvent was codistilled with toluene. The crude residue was purified by column chromatography (1:1 EtOAc–hexane) to give the pure orthoester.

1',2,3,3',4',6'-Hexa-O-acetyl-4,6-O-acrylidenesucrose (**1**).—Yield, 20%; mp 112–114°C; $[\alpha]_D^{20}$ 53° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.50 (m, 7 H, H-1,3,3',4',8,9), 4.83 (dd, 1 H, H-2), 3.40 (q, 2 H, OEt), 2.10 (m, 18 H, OAc), and 1.20 (t, 3 H, OEt); ^{13}C NMR ($CDCl_3$): δ 170.3, 170.2, 169.8 (OAc), 133.26, 119.16 (C-8,9), 109.8 (C-7), 104.08 (C-2'), 90.63 (C-1), 58.7 (OEt), 20.6 (OAc), and 14.9 (OEt). Anal. Calcd for $C_{29}H_{40}O_{18}$: C, 51.4; H, 6.06. Found: C, 51.3; H, 5.94.

1',2,3,3',4',6'-Hexa-O-acetyl-4,6-O-(2-bromo-1-methoxypropylidene)sucrose (**2**).—Yield, 40%; mp 61–63°C; $[\alpha]_D^{20}$ 47° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.70 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.45 (m, 3 H, H-3,3',4'), 4.85 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.15 (m, 7 H, H-4,5,6,8,1',5',6'), 2.15 (m, 18 H, OAc), 1.66 (d, 3 H, $J_{8,9}$ 7 Hz, H-9,9',9''), and 1.30 (t, 3 H, OEt); ^{13}C NMR ($CDCl_3$): δ 170.5, 170.3, 170.2, 169.9, 169.8 (OAc), 111.2 (C-7), 103.95 (C-2'), 90.3 (C-1), 53.8 (OEt), 46.4 (C-8), 21.6 (C-9), 20.7, 20.3 (OAc), and 14.9 (OEt). Anal. Calcd for $C_{29}H_{41}BrO_{18}$: C, 45.97; H, 5.7; Br, 10.53. Found: C, 46.22; H, 5.4; Br, 10.6.

1',2,3,3',4',6'-Hexa-O-acetyl-4 (or 6) O-acryloylsucrose (**3**) *and 1',2,3,3'4',6'-hexa-O-acetyl-4 (or 6) O-(2-bromopropionyl)sucrose* (**4**).—Aq acetic acid (20%) was added to a solution of compound **1** (respectively, **2**) in EtOAc. This heterogeneous mixture was stirred vigorously during 20 h at room temperature. The reaction was monitored by TLC (1:1 EtOAc–hexane). The organic layer was then neutralized (Na_2CO_3), filtered, dried, and the solvent was evaporated. The amorphous residue was then purified by column chromatography (1:1 EtOAc–hexane) to give pure **3** (or **4**) in 50% yield.

Data for **3**: yield, 50%; mp 53–55°C; $[\alpha]_D^{20}$ 46° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$); δ 6.30, 5.90 (2 m, 3 H, H-8,9,9′), 5.60 (d, 1 H, H-1), 4.75 (dd, 1 H, $J_{1,2}$ 10 Hz, H-2), 5.40 (m, 3 H, H-3,3′,4′), 2.10 (m, 18 H, OAc), and 2.95 (s, 1 H, OH); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.9, 170.4, 170.2, 170.0, 169.8 (OAc), 166.6 (C=C–*C*O–O), 132.9, 131.8 (C-9), 127.9, 127.2 (C-8), 104.3 (C-2′), 90.4 (C-1), and 20.6 (OAc). Anal. Calcd for $C_{27}H_{36}O_{18}$: C, 49.90; H, 5.70. Found: C, 49.74; H, 5.51.

Data for **4**: yield, 50%; mp 50–52°C; $[\alpha]_D^{20}$ 50° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.80 (d, 3 H, $J_{9,10}$ 7 Hz, H-10,10′,10″), 2.10 (m, 18 H, OAc), 3.75 (s, 1 H, OH), 4.40 (m, 6 H, H-1′,4,5,5′,6′,9), 4.80 (dd, 1 H, H-2), 5.40 (m, 3 H, H-3,3′,4′), and 5.65 (d, 1 H, H-1); ^{13}C NMR ($CDCl_3$): δ 171.1–169.7 (OAc), 104.3 (C-2′), 90.4 (C-1), 39.8 (C-9), 21.6 (C-10), and 20.9, 20.6 (OAc). Anal. Calcd for $C_{27}H_{37}BrO_{18}$: C, 44.44; H, 5.07; O, 39.50. Found: C, 44.77; H, 4.92; O, 39.51.

4-O- and 6-O-Acryloylsucrose (**5**).—Compound **3** was treated with a catalytic amount of NaOMe in MeOH at room temperature for 3 h to give pure, crystalline **5**: $[\alpha]_D^{20}$ 49° (*c* 1.0, $CHCl_3$); ^1H NMR (D_2O): δ 6.30 (m, 3 H, H-8,9,9′) and 5.50 (d, 1 H, H-1).

Direct synthesis of 4-O- and 6-O-acryloylsucrose (**5**).—To a suspension of sucrose in anhyd *N*,*N*-dimethylformamide stirred at room temperature were added 1.5 mol equiv of triethyl orthoacrylate and a catalytic amount of pyridinium *p*-toluenesulfonate. After 20 h, water (10% of the volume of the organic solvent) and an additional amount of pyridinium *p*-toluenesulfonate were added. The solution was stirred at room temperature during several h, and the reaction was monitored by TLC (5:3:2 butanol–EtOH–water). The solution was then neutralized with Na_2CO_3, filtered, the solvent was evaporated, and the water was codistilled with toluene. The acrylate derivative may be isolated by flash-column chromatography (12:3:2 EtOAc–EtOH–water) in 25% yield. The crude material containing sucrose and its acryloyl derivative can be used in polymerization reactions by the sequence of dissolution in water, washing several times with 1:1 acetone–CH_2Cl_2, and then the water was codistilled with toluene.

Synthesis of 4(or 6)-O-acetyl-4(or 6)-O-acryloyl 1′,2,3,3′,4′,6′-hexa-O-deuteroacetylsucrose (**6**).—To a suspension of sucrose in anhyd *N*,*N*-dimethylformamide stirred at room temperature were added 1.5 mol equiv of triethyl orthoacrylate and a catalytic amount of pyridinium *p*-toluenesulfonate. After 20 h, the solution was neutralized with Na_2CO_3, filtered, and the solvent was evaporated under reduced pressure. The residue was acetylated in pyridine at 0°C with deuteromethyl acetic anhydride (16 mol equiv). After the usual workup and evaporation of the solvents, the crude acetylated residue was purified by column chromatography to give the pure orthoester. The latter was then hydrolysed in water containing pyridinium *p*-toluenesulfonate as previously described. The resulting ester was then acetylated in the usual way with acetic anhydride to give **6**, which was used without further purification.

Homopolymerization of **3**.—Component **3** (1 g) was dissolved in toluene, and, after removal of oxygen by a stream of nitrogen, AIBN (5 mg) was introduced. The

solution was stirred for 24 h at 60°C. The polymer was precipitated into EtOH, filtered, washed several times with EtOH, and dried in vacuum at 40°C.

Homopolymerization of **5**.—Compound **5** (0.7 g) or a mixture of **5** and sucrose (3 g) was dissolved in water, and the solution was sparged with nitrogen. Potassium persulfate (1 mol%) was then added, and the solution was stirred at 60°C for 24 h. The resulting poly(sucrose acrylate) was recovered by precipitation with acetone, filtered, dialysed to eliminate residual sucrose, and finally dried under vacuum at 40°C.

Copolymerization of **3** *with styrene.*—Compound **3** (1 g) and styrene (0.48 g) were dissolved in toluene, and oxygen was removed by a stream of nitrogen. AIBN (10 mg) was then added, and copolymerization was carried out at 70°C for 12 h. The polymerization was stopped by pouring the reaction mixture into EtOH. The copolymer was then filtered, washed several times with EtOH, and dried in vacuum at 60°C.

Copolymerization of **5** *with styrene.*—The general method was as follows; a mixture of **5** and sucrose was first dissolved in *N*,*N*-dimethylformamide (1.5–3.5 mol L^{-1}) before adding styrene. AIBN (1 mol%) was then introduced and the solution was flushed with nitrogen. The polymerization reaction was carried out under stirring at 70°C for 24 h. Copolymers that were insoluble in water were precipitated in ether, filtered, washed several times with water to eliminate sucrose and then with acetone, and finally dried under vacuum at 40°C. Water-soluble copolymers were precipitated in acetone, filtered, dialysed, and dried in vacuum at 40°C.

ACKNOWLEDGMENTS

This work was carried out with the financial support of Béghin-Say and the Centre National de la Recherche Scientifique within the framework of the Groupement Scientifique "Sucrochemistry".

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