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Amphiphilic copolymers of sucrose methacrylate and acrylic monomers: Bio-based materials from renewable resource

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ABSTRACT

Regioselective sucrose 1′-*O*-methacrylate obtained by transesterification catalyzed by Proteinase-N was copolymerized with hydrophilic N-isopropylacrylamide and hydrophobic methyl methacrylate in different molar ratios by free radical polymerization. The copolymers were characterized by ^{13}C nuclear magnetic resonance spectroscopy, gel permeation chromatography, differential scanning calorimetry and thermogravimetry. Solubility and phase behavior of aqueous solutions were also investigated. The glass transition of the copolymers presents a positive deviation from the values of the homopolymers due to the high density of inter and intramolecular hydrogen bonding. Their solubility is strongly dependent on the composition. Copolymers poor in methyl methacrylate are water soluble, while copolymers richer in methyl methacrylate behaves as hydrogel. These hydrogels are not chemically crosslinked and their form can be design prior swelling by the conventional processing methods, such as solvent casting and extrusion for instance. Copolymers of N-isopropylacrylamide are water soluble and their aqueous solutions present a lower critical solution temperature behavior forming thermoreversible hydrogels.

1. Introduction

The use of sucrose as raw material has attracted special attention for the production of surfactants (Carrea, Riva, Secundo, & Danieli, 1989; Hass et al., 1959; Wada, Onuma, Ushikubo, & Ito, 1988) and bio-based polymers (Chen et al., 1995; Chen & Park, 2000; Cheng & Gross, 2010; Crucho, Petrova, Pinto, & Barros, 2008; Feng et al., 2010; Jhurry et al., 1992; Liu & Dordick, 1999; Patil, Dordick, & Rethwisch, 1991a, 1991b, 1996; Patil, Li, Rethwisch, & Dordick, 1997; Zamora, Strumia, & Bertorello, 1996) for several reasons. First, sucrose is a cheap raw material obtained directly from sugar cane and sugar beets. According to the Brazilian Ministry of Agriculture, the world production of sugar cane in 2007 was 1558 million tons, resulting in a total production of 166.3 million tons of sugar, among other products (Strapasson et al., 2009). Second, sucrose is a reactive molecule having eight free hydroxyl groups and two anomeric carbon atoms. This enables several chemical transformations. However, some strategies are required to guarantee the reaction selectivity towards the desired products. In general, two synthetic strategies are employed: (1) enzymatic catalysis and (2) chemical catalysis. The latter requires protection–deprotection of the functional groups, what is not favorable in the context of green chemistry, in which the reduction of derivatives is one of its principles. On the other hand, enzymatic reactions are very selective and provide high yields of alkylglucosides that have aroused great interest as the main synthetic route for modified saccharides (Cheng & Gross, 2010; Dordick, 1992; Klibanov, 1986; Rich, Bedell, & Dordick, 1995; Riva, Chopineau, Kieboom, & Klibanov, 1988).

Among the numerous derivatives of sucrose, the ones containing vinyl or acrylic groups were of particular interest in this work. These monomers contain reactive carbon-double bonds, allowing radical polymerization, which is usually not only relatively simple to perform but also provides high yields of polymers with low polydispersities (1.5–2.0) and high molecular weight. Moreover, the monomers derived from sucrose are strongly hydrophilic. The combination of these monomers with hydrophobic ones (e.g., methyl methacrylate) can lead to amphiphilic copolymers with a wide range of properties and applications. Typically, amphiphilic polymers, such as sugar-based polymers, are widely used in applications that require biocompatibility and/or biodegradability (Barros, Petrova, & Singh, 2010; Cheng & Gross, 2010; Feng et al., 2010; Galgali, Puntambekar, Gokhale, & Varma, 2004; Miura, 2007; Patil et al., 1997; Shantha & Harding, 2002; Takasu, Baba, & Hirabayashi, 2008).

The first reports on "saccharide polymers" mostly described the use of these materials for the production of polymeric networks (Chen & Park, 2000; Liu & Dordick, 1999; Patil et al., 1996, 1997; Zamora et al., 1996). This is due to the difficulties in obtaining acrylic and vinyl saccharide monomers with a high

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Table 1
Reaction yield (Y), nominal molar composition (C_N) and determined by ^{13}C NMR (C_{NMR}), apparent number average molar weight (M_n), apparent weight average molar weight (M_w) and polydispersity (M_w/M_n) determined by GPC for polymers.

Entry	Sample	f_{SMA}	Y (%)	C_N	C_{NMR}	M_n(g mol^{-1})	M_n (g mol^{-1})	M_w M_n
1	PMMA	0.00	100	–	–	215,000	334,000	1.6
2	P(SMA-*co*-MMA) 1–20	0.17	100	1–20	nd	385,000	725,000	1.9
3	P(SMA-*co*-MMA) 1–10	0.29	100	1–10	nd	262,000	385,000	1.5
4	P(SMA-*co*-MMA) 1–5	0.45	99	1–5	1.0–7.0	410,000	749,000	1.8
5	P(SMA-*co*-MMA) 1–3	0.58	90	1–3	1.0–3.0	428,000	788,000	1.8
6	P(SMA-*co*-MMA) 1–1	0.80	95	1–1	1.0–1.0	268,000	393,000	1.5
7	PSMA	1.00	100	–	–	430,000	802,000	1.9
8	P(SMA-*co*-NIPAAm) 1–1	0.78	93	1–1	1.0–1.0	316,000	822,000	2.6
9	P(SMA-*co*-NIPAAm) 1–3	0.55	71	1–3	1.0–1.0	259,000	478,000	1.9
10	P(SMA-*co*-NIPAAm) 1–5	0.42	78	1–5	1.0–6.5	546,000	1,330,000	2.4
11	P(SMA-*co*-NIPAAm) 1–10	0.27	64	1–10	1.0–5.3	369,000	673,000	1.8
12	P(SMA-*co*-NIPAAm) 1–20	0.15	41	1–20	1.0–20.0	479,000	957,000	2.0
13	PNIPAAm	0.00	78	–	–	181,000	278,000	1.5

mono-to-polysubstituted ratio. The enzymatic catalysis is a powerful way to obtaining sucrose-based monomers. Lipase has been described in the literature as an efficient enzymatic catalyst to esterification of sucrose. However, the selectivity of lipase-catalysed esterifications of sucrose takes place at the 6-OH and 6′-OH hydroxyl groups (Oosterom et al., 1996; Queneau, Jarosz, Lewandowski, & Fitremann, 2008), making the lipases catalysis an important way to obtain diesters of sucrose as precursors to polyesters in which the sucrose derivatives constitute the backbone of the polymers (Albertin, Stenzel, Barner-Kowollik, Foster, & Davis, 2004). Sucrose-based polyester (Park, Kim, & Dordick, 2000) and polyamides (Patil et al., 1991a), in which sucrose is a side group, were synthesized using lipases Novozym-435 enzymatic catalysis and Proleather enzymatic catalysis, respectively. In these cases the monomer synthesis step catalyzed by lipases Novozym-435 presented low yield for the monosubstituted derivative (28% after 5 days and low mono-to-polysubstituted derivatives ratio). In the present work the synthesis of the sucrose monomer, sucrose 1′-*O*-methacrylate (SMA), was based on the protease-catalyzed esterification route of sucrose described in the literature (Potier, Bouchu, Descotes, & Queneau, 2000, 2001). This synthetic route displays high yields and high mono-to-polysubstituted derivatives ratios because of the higher selectivity at the 1′-OH hydroxyl group in comparison with 6-OH and 6′-OH hydroxyl (Potier et al., 2001). The monosubstituted sucrose monomer was copolymerized with N-isopropylacrilamide (NIPPAm) and with methyl methacrylate (MMA) aiming to obtain amphiphilic copolymers by conventional free radical polymerization. The solubility, glass transition temperature and aqueous solution behavior showed to be dependent on the copolymers composition and on the hydrophobicity of the comonomers NIPPAm and MMA, as will be discussed.

2. Materials

The chemicals 2,2,2-trifluoroethylmethacrylate (TFEM), sucrose, *N*-isopropylacrylamide (NIPAAm), benzoyl peroxide (BPO) and the enzyme Proteinase-N from *Bacillus subtilis* (ca. 6 U/mg) were supplied by Sigma–Aldrich (USA). Methyl methacrylate (MMA) was from Hoechst. The solvents *N*,*N*-dimethylformamide (DMF), diethyl ether, ethyl acetate, methanol (MeOH), acetone (Me_2CO), chloroform and methylene chloride (CH_2Cl_2) were purchased from Synth (Brazil).

DMF and MMA were distilled and stored with pre-activated molecular sieves 5 A. BPO was dried under vacuum overnight before use. Proteinase-N was prepared by dissolving the crude enzyme in water (5 mg mL^{-1}), adjusting the pH to 10.0 with 0.1 mol L^{-1} KOH and then freeze-drying the solution. The other chemicals and solvents were used without further purification.

3. Experimental

3.1. Sucrose 1′-O-methacrylate (SMA) synthesis

The monomer synthesis was based on the methodology described in the literature (Potier et al., 2000, 2001). The reaction mixture consisting of sucrose (1.5 g, 4.4 mmol), TFEM (3.00 mL, 21.1 mmol), Proteinase-N (660 mg) and DMF–H_2O (v_{H_2O}/v_{tot} = 7%, 11.1 mL) in a closed tube was heated at 45 °C under magnetic stirring at 250 rpm for 1 day. The enzyme was separated from the reaction mixture by filtration and the solution was concentrated under vacuum. The purification of SMA was carried out by silica-gel (mesh 230–400 – Macherey-Nagel) Flash Chromatography (FC) with CH_2Cl_2/Me_2CO/MeOH/H_2O 56/20/20/4 (v/v) solvent system as eluent (SMA R_f = 0.24). The desired aliquots were concentrated under vacuum to obtain a white foam with 70% regioisomeric yield OH-1′ after purification by FC. This product was characterized by ^1H and ^{13}C NMR spectroscopies in D_2O (Acros) and the obtained data were compared with the literature.

3.2. Polymer synthesis

For the polymerization reactions, solutions 20 wt% of purified SMA and comonomer in *N*,*N*-dimethylformamide (DMF) (10–15 mL) were prepared. The comonomers employed were methyl methacrylate (MMA) and *N*-isopropylacrylamide (NIPAAm), in molar ratios SMA/comonomer 1:1, 1:3, 1:5, 1:10 and 1:20. The homopolymers of SMA, MMA and NIPAAm were also synthesized. The polymerization was initiated upon adding 0.1% (mol/mol) of benzoyl peroxide (BPO). This solution was added in an ampoule and subjected to cycles of freezing/degassing to eliminate dissolved molecular oxygen, a radical inhibitor. The polymerization was carried out at 60 °C under nitrogen atmosphere for 6 days. The product was precipitated in a nonsolvent (diethylether: Table 1, entries 1–7; ethyl acetate: Table 1, entries 8–13) and dried under vacuum at 40 °C. The polymers were purified by dialysis to remove non-reacted monomers.

3.3. Polymer characterization

The ^1H nuclear magnetic resonance (^1H NMR) spectra of the copolymers showed an intense overlap of the signals of the monomers making the quantitative analyses very difficult. Because of this ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy was adopted to determine the composition of the copolymers. ^{13}C NMR spectra of polymer solutions 100 mg mL^{-1} in DMF-d7 (Aldrich – Table 1, entries 1–7), using the carbonyl of DMF-d7 at 163.15 ppm as internal standard, and D_2O (Acros – Table 1, entries 8–13), using