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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 ($\upsilon_{H_2O}/\upsilon_{tot} = 7\%$, 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 ^{1}H 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 ^{1}H nuclear magnetic resonance (^{1}H 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

CCl_4 as external standard, in 5 mm RMN tubes, were obtained on a Varian Inova-500 (500 MHz) spectrometer. In order to guarantee a quantitative analysis the nuclear Overhauser enhancement in the ^{13}C NMR spectra was suppressed by inverse gated decoupling. The pulse angle used was 45°, acquisition time was 1 s, the interval between pulses was 10 s and the spectral width was 35,000 Hz.

The apparent number–average molecular weight (M_n), apparent weight–average molecular weight (M_w) and molecular weight distribution of the polymers were determined using gel permeation chromatography (GPC), which was performed on a Viscotek GPCmax VE 2001 equipment, equipped with Viscotek VE 3580 RI and Viscotek UV 2500 detectors, Viscotek TGuard 10 × 4.6 mm guard column and 3X Viscotek T6000 M 300 × 7.8 mm (10 μm particles) columns. The column system was heated at 60 °C. LiBr 10 mmol L^{-1} solution in DMF was used as eluent at a flow rate of 1.0 mL min^{-1}. The polymer solutions of 8.0 mg mL^{-1} were prepared with this eluent solvent and volumes of 100 μL were injected. Molecular weights are relative to polystyrene (PS) standards (Viscotek) with molecular weights from 1050 to 3,800,000 g mol^{-1}.

Differential scanning calorimetry (DSC) was employed to determine the glass transition temperature of the copolymers on a DSC 2910 TA instruments calorimeter, at 20 °C min^{-1} heating rate under an argon atmosphere. Analysis program: (1) heating from 25 °C to 200 °C; (2) isotherm for 1 min; (3) cooling from 200 °C to −50 °C; (4) isotherm for 5 min; and (5) heating from −50 °C to 200 °C. Samples were carefully dried before DSC experiments. Moreover, a small hole had been made in the sample pan used in the experiments allowing the evaporation of any sorbed water during the first heating scan. The thermal stability of the polymers was determined by thermogravimetric analysis (TGA) on a TGA 2950 TA instruments thermo-balance under an argon atmosphere (100 mL min^{-1} flow rate) at 10 °C min^{-1} heating rate from 30 °C to 600 °C.

3.4. Polymer-solvent studies

To assess the solubility of the polymers in water (Milli-Q), chloroform, methanol and DMF at 25 °C, 100 μL of solvent was added to 10 mg of powdered polymer sample. After 4 h a new aliquot of solvent (100 μL) was added until a clear solution was observed.

In order to evaluate the swelling ratio of the polymers, around 20 mg of polymeric films of the copolymers were immersed into water (3 mL) at 25 °C for 48 h. After this, the weight of the swollen polymer was measured.

Phase behavior of the polymer in aqueous solution was determined by turbidity measurements. These measurements were performed with aqueous polymeric solutions of 0.1 wt% (Milli-Q water) in quartz cells (1.0 cm optical length) with a HP-Agilent 8453 spectrophotometer, equipped with a Peltier heating system and a HP-Agilent 89090A temperature controller system, at 300 nm wavelength from 10 °C to 90 °C. The temperature was increased using a dynamic temperature step program with temperature increments of 3.0 °C and isothermal holds of 1 min at each new temperature before the measurement. After this measurement, a new one was performed with temperature increments of 0.5 °C in the range of temperature close to the thermal event. The results presented in this work correspond to the latter experiments.

4. Results and discussion

Sucrose 1′-*O*-methacrylate (SMA) was obtained in yields up to 70% after 1 day of reaction and after purification while yields for disubstituted are lower than 4%. Although high yields were obtained for the monosubstituted monomer, these are lower than that reported in the literature (Potier et al., 2001). This difference can be easily understood since the value of 70% for yield corresponds to purified monomer, what is not the case for the work presented by Potier et al. (2001). In addition, enzyme/sucrose ratio used in the present work was 0.44, against 0.60 as reported in the article of Potier et al. (2001). Finally, the reaction scale adopted in the present work is 60 times higher and our previous studies showed that the increase of the reaction scale leads to a decrease of yield and selectivity for sucrose 1′-*O*-methacrylate (data not shown). Thus, the synthetic route and conditions adopted to obtain sucrose 1′-*O*-methacrylate were adequate to the purpose of the work.

Table 1 summarizes the yield of the polymerization for each polymer composition. High yields of copolymers consisting of SMA and methyl methacrylate (MMA) were obtained (Table 1, entries 2–6). This reveals no significant difference in the reactivity of these monomers under the reaction conditions. For the copolymers of SMA and *N*-isopropylacrylamide (NIPAAm), an increase of NIPAAm in the reaction mixture results in lower yields of copolymers (Table 1, entries 8–12). Moreover, the yield of poly(*N*-isopropylacrylamide) (PNIPAAm) is lower than the yield of poly(sucrose 1′-*O*-methacrylate) (PSMA) and poly(methyl methacrylate) (PMMA). This suggests that NIPAAm has the lowest reactivity among the three above-mentioned monomers.

The composition of the copolymers listed in Table 1 was determined by ^{13}C NMR spectroscopy. For this purpose the reference signals for SMA (C2′) at 103 ppm, MMA ($-O-CH_3$) at 52 ppm and NIPAAm (CH isopropyl group) at 42 ppm were used. For copolymers richer in SMA (Table 1, entries 4–6), the results are close to the monomer ratio in the reaction medium and consistent with expected values. However, determination of the composition of the copolymers rich in MMA was not possible (Table 1, entries 2 and 3) due the low signal-to-noise ratio for the signals of SMA in these samples. On the contrary, for the copolymers P(SMA-*co*-NIPAAm), a good signal-to-noise ratio was observed for the signals of SMA even at high fractions of NIPAAm.

The apparent molecular weight and the polydispersity of the polymers were determined by GPC using polystyrene (PS) standards (Table 1). In general, the copolymers were obtained with high molecular weight (around 10^5 g mol^{-1}) and polydispersities ranging from 1.5 to 1.9 (Table 1, entries 2–6) for the P(SMA-*co*-MMA) copolymer series and from 1.8 to 2.6 (Table 1, entries 8–12) for the P(SMA-*co*-NIPAAm) copolymers. The higher polydispersities of the copolymers of NIPAAm and SMA is probably associated to the difference in the reactivity of the two monomers and also to the termination mechanism of the polymerization in both cases (Ozizmir & Odian, 1980). This leads to the formation of the polymeric chains over a broad range of rates, causing the broadened distribution of molecular weight.

Fig. 1 shows the DSC curves (second heating scan) for the SMA copolymers with MMA or NIPAAm. They exhibit a single glass transition. Table 2 lists the values of the temperature of glass transition (T_g), glass transition width (ΔT_g = difference between the onset and endset temperatures of the glass transition, expressed in °C) and heat capacity variation (ΔC_p) involved in the glass transition.

Fig. 2 presents the correlation curves between the glass transition temperature and composition (weight fraction of SMA). All copolymers present a single glass transition, indicating a random distribution of the monomers in the chain. Some miscible polymer blends and random copolymers display an additive effect on the temperature of glass transition with respect to the temperatures of glass transition of the homopolymers (Olabisi, Robeson, & Shaw, 1979), as indicated by the dashed lines in Fig. 2. Positive deviations of T_g of the copolymers in relation to the values of the corresponding homopolymers, as the ones seen in Fig. 2, suggests strong intermolecular interactions between the constituents of the polymer blends or copolymers (Olabisi et al., 1979). Intra and inter-interactions are shown in Fig. 3: hydrogen bonds between the

Table 2
Glass transition temperature (T_g), width (ΔT_g) and heat capacity variation (ΔC_p) associated to the glass transition, solubility (*S*) and swelling degree (*I*).

Entry	Material	T_g (°C)	ΔT_g (°C)	ΔC_p(J g^{-1} °C^{-1})	H_2O	MeOH	$CHCl_3$
					I (%)	*I* (%)	*I* (%)
1	PMMA	116	32	0.30	101 ± 5	111 ± 6	*S*
2	P(SMA-*co*-MMA) 1–20	129	22	0.28	104 ± 5	130 ± 7	*S*
3	P(SMA-*co*-MMA) 1–10	132	25	0.38	107 ± 5	132 ± 7	*S*
4	P(SMA-*co*-MMA) 1–5	132	38	0.39	134 ± 7	193 ± 10	117 ± 6
5	P(SMA-*co*-MMA) 1–3	133	38	0.43	282 ± 14	184 ± 9	112 ± 6
6	P(SMA-*co*-MMA) 1–1	118	39	0.42	*S*	161 ± 8	113 ± 6
7	PSMA	116	22	0.42	*S*	115 ± 6	113 ± 6
8	P(SMA-*co*-NIPAAm) 1–1	175	20	0.30	*S*	168 ± 8	108 ± 5
9	P(SMA-*co*-NIPAAm) 1–3	186	14	0.30	*S*	180 ± 9	108 ± 5
10	P(SMA-*co*-NIPAAm) 1–5	143	24	0.43	*S*	*S*	116 ± 6
11	P(SMA-*co*-NIPAAm) 1–10	143	26	0.48	*S*	*S*	407 ± 20
12	P(SMA-*co*-NIPAAm) 1–20	144	15	0.54	*S*	*S*	473 ± 24
13	PNIPAAm	131	13	0.45	*S*	*S*	*S*

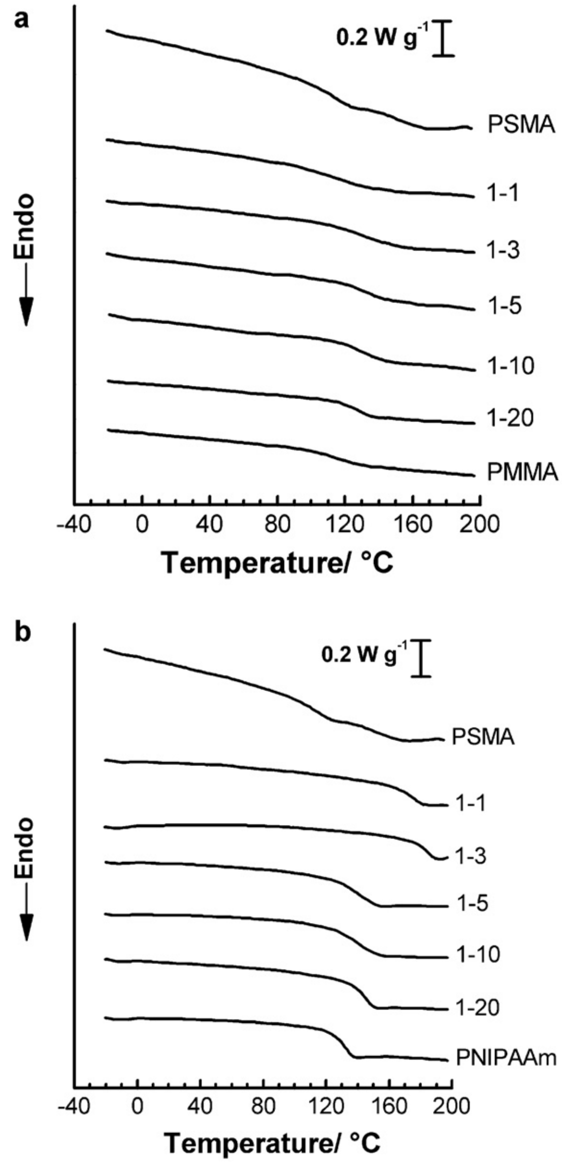

Fig. 1. DSC curves (second heating scan) for: (a) P(SMA-*co*-MMA) and (b) P(SMA-*co*-NIPAAm).

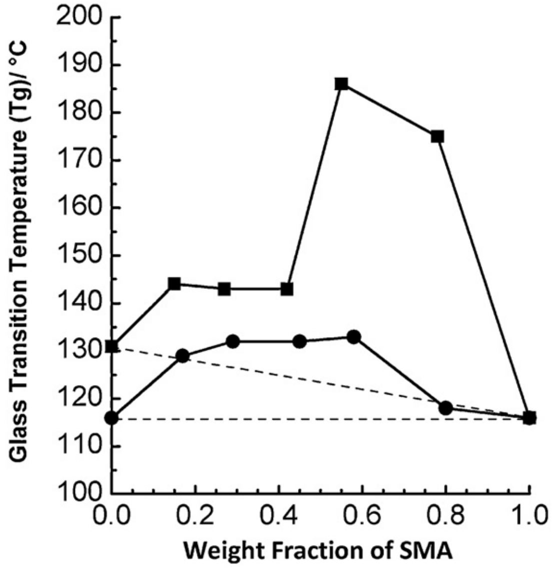

Fig. 2. Glass transition temperature as a function of weight fraction of SMA in the copolymers with MMA (●) and NIPAAm (■).

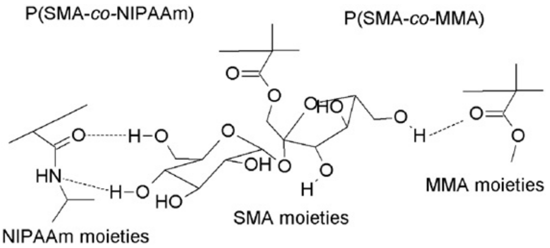

Fig. 3. Hydrogen bond interactions between the segments in the copolymers.

hydroxyl groups of SMA and the carbonyl groups of MMA in the case of P(SMA-*co*-MMA) copolymer and the intermolecular hydrogen bonds established between the hydroxyl groups of SMA and N- and O-sites of the amide groups of NIPAAm for the P(SMA-*co*-NIPAAm) copolymers.

The higher density of hydrogen bonds, caused by the nature of the amide group of NIPAAm, is probably the reason of the more pronounced positive effect seen in Fig. 3, when compared with the glass transition temperature of P(SMA-*co*-MMA) copolymers.

Fig. 4 shows thermogravimetric curves for the P(SMA-*co*-MMA) series under an inert atmosphere. The first thermal event (200–230 °C) corresponds to the cleavage of head-to-head bonds, resulting in free radical and unsaturated terminations. As a

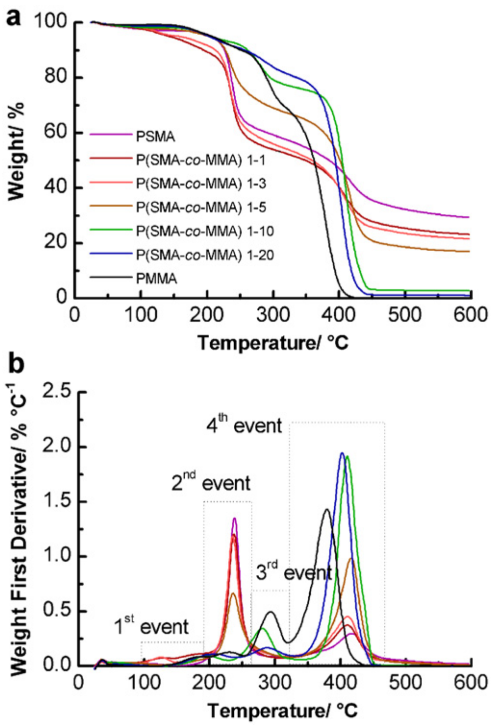

Fig. 4. (a) Thermogravimetric curves and (b) their first derivative for PSMA, PMMA and copolymers P(SMA-*co*-MMA) (heating rate of 10 °C min^{-1} under an argon atmosphere).

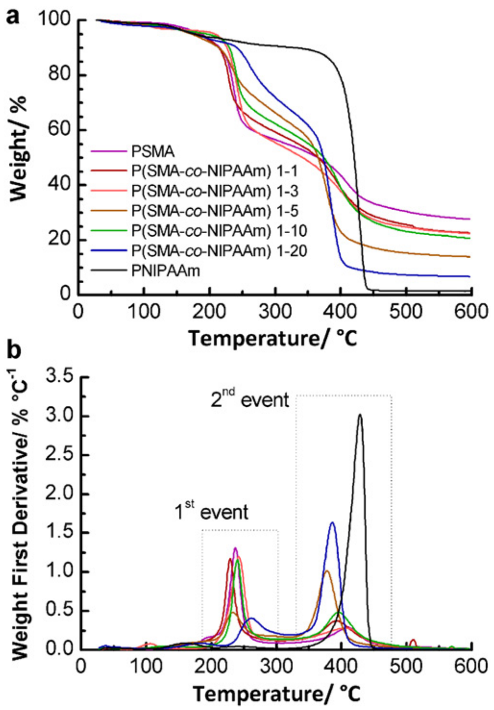

Fig. 5. (a) Thermogravimetric curves and (b) their first derivative for PSMA, PNIPAAm and copolymers P(SMA-*co*-NIPAAm) (heating rate of 10 °C min^{-1} under an argon atmosphere).

consequence, the thermal stability of the whole polymer chains decreases markedly leading to the subsequent depolymerization (Higashi, Shiba, & Niwa, 1989). In the second stage of thermal degradation (240 °C), the weight loss increases with the SMA content in the copolymers. This was due to the release of water molecules derived from the condensation of hydroxyl side groups of the SMA, as well as the pyrolysis of the saccharide groups. The third event (280–290 °C) is related to the cleavage of unsaturated terminations involving homolytic β-cleavage (Manring, 1989). The fourth event (380–420 °C) results from random cleavages of the carbon skeleton (Manring, 1991).

The P(SMA-*co*-NIPAAm) copolymers show only two events upon thermal degradation, as seen in Fig. 5. The first event is associated with degradation of the SMA side groups, as described previously. The second event is assigned to the random cleavage of the polymeric chain into oligomers with simultaneous degradation of the side groups segments of NIPAAm (Schild, 1996). For both series of copolymers an increase of the fraction of SMA results in a higher amount of residual material due to the crosslinking between hydroxyl groups of SMA moieties.

Table 2 summarizes the results of the solubility and swelling tests. While the solubility tests are qualitative, the swelling tests are quantitative and expressed in terms of percent weight of swollen polymer compared to the dry polymer.

The materials listed in Table 2 are soluble in polar solvents, such as DMF, DMSO and *N*-methyl-2-pyrrolidone (NMP), indicating the absence of extensive crosslinking, as desired. Both series of copolymers show an amphiphilic character strongly dependent on the copolymer composition. While the PSMA and PNIPAAm are water soluble, PMMA is soluble in organic solvents, such as chloroform. Only the copolymer P(MMA-*co*-SMA) 1–1 (Table 2, entry 6), the one that is richest in SMA, is soluble in water, while the other copolymers of this series only swell in water resulting in hydrogels that are not chemically crosslinked. The amount of absorbed water increases with the fraction of SMA. The copolymer P(MMA-*co*-SMA)1–3 (Table 2, entry 5) presents a high swelling degree in water. The opposite effect is observed when water is replaced with chloroform, i.e. the copolymers rich in MMA (Table 2, entries 2 and 3) display high swelling degrees in chloroform, while PMMA is soluble in this solvent. In methanol, the swelling of materials richer in MMA happens to a greater extent than in water, while the opposite effect is seen for materials richer in SMA.

Aqueous PNIPAAm solutions present phase diagrams with Lower Critical Solution Temperature (LCST) behavior, forming thermoreversible gels at temperatures above this minimum point. As this phenomenon is accompanied by turbidity of the solution, the measurement of transmittance as a function of temperature can be used to determine the temperature of phase segregation in solutions of this class of materials. The results obtained in the study of

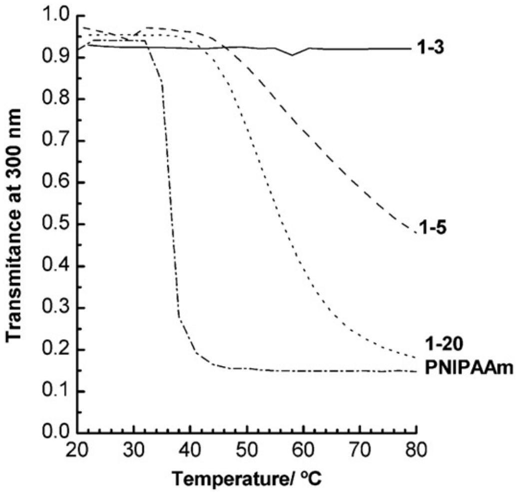

Fig. 6. Transmittance curves at 300 nm as function of temperature for aqueous polymer solutions: P(SMA-*co*-NIPAAm) 1–3 (—), P(SMA-*co*-NIPAAm) 1–5 (-·-),P(SMA-*co*-NIPAAm) 1–20 (····) and PNIPAAm (-···-).

phase behavior for water-soluble P(SMA-*co*-NIPAAm) copolymers are displayed in Fig. 6. Only the PNIPAAm and the P(SMA-*co*-NIPAAm) 1–5 and 1–20 copolymers presented continuous decay of the transmittance with increasing temperature (the turbidimetric curves for the other copolymers solutions are not show in Fig. 6), which can be attributed to LCST behavior. For these aqueous copolymer solutions phase segregation occurs at 32.5 ± 0.5, 37.0 ± 0.5 and $41.0 \pm 0.5\,^{\circ}$C, respectively. The decrease of the values of the transmittance is caused by the light scattering resulting from the turbidity of the polymeric solution above the LCST point. As the turbidity gradually disappears on cooling the solution, this process can be considered reversible. The results also show that the increase of the hydrophilic character of the copolymer, upon changing NIPAAm with SMA, results in a high temperature of phase segregation.

5. Conclusions

In summary, the regioselective synthesis of sucrose 1′-*O*-methacrylate (SMA) monomer was achieved. The desired sucrose-derived monomer was obtained in yields above 70% for the purified product. The work-up of the reaction mixture was essential for the removal of difunctionalized-sucrose methacrylate by-products. This is crucial to obtain non-crosslinked amphiphilic copolymers. The linear amphiphilic copolymers were synthesized in high yields. The copolymers showed molecular weights about $10^5\,\mathrm{g\,mol^{-1}}$. The physical–chemical properties of these materials were studied. The results showed that the thermal degradation, temperature of glass transition, solubility, swelling and phase behavior in aqueous solution change markedly with the copolymer composition. Copolymers composed of NIPAAm and SMA showed LCST behavior in aqueous solution. An increase of the temperature of phase segregation and subsequent formation of a thermoreversible hydrogel with increasing SMA content in the copolymers P(SMA-*co*-NIPAAm) is observed. Polymers with similar behavior have been employed in drug delivery systems. As an advantage, the polymers synthesized in the present work are potentially biodegradable and come (at least partially) from renewable resources. Although LCST behavior was not observed for the amphiphilic copolymer consisting of MMA and SMA, the materials rich in SMA showed high swelling in water (130–280 wt%), characterizing them as hydrogels. These kinds of materials are interesting for applications such as absorbents and as bandages for skin treatments.

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