

Preparation of unsaturated polyesters using boric acid as mild catalyst and their sulfonated derivatives as new family of degradable polymer surfactants

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ABSTRACT

Boric acid-pyridine mixture is presented as mild catalyst for polycondensation of semi-esters of ethylene glycol, in situ-generated by “cyclic anhydride–diol” reaction scheme from maleic, succinic and phthalic anhydrides. This catalyst system was demonstrated to give colorless polyesters in low molecular weights (Mn: 1650–1950 Da) within 4 h at 130 °C ¹H NMR spectra of the polyesters derived from maleic anhydride revealed significant isomerization of maleate groups to fumarate units (80 %) during the polyesterification. Maleate and fumarate double bonds of the unsaturated polyesters (USP) were demonstrated to add bisulfite ions quantitatively to give sulfonated polyesters. The resulting sulfonated polyesters with 50% and 70% succinate units exhibited relatively narrow size spherical and ellipsoidal micelles in aqueous solutions, as inferred from surface tension, DLS and ESEM measurements. The results showed that, this procedure allows preparing a new family of polymer surfactants with tunable hydrophilicity and degradable polyester backbones.

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1. Introduction

Low molecular weight unsaturated polyesters (USP) (i.e. 1800–2500 Da) constituting with maleate/fumarate segments in the backbone are versatile family of thermosetting materials having extensive use in glass-fiber reinforcement etc. Solutions of the USP in suitable vinyl monomers such as styrene are under marketing to produce concrete-like polymer composites with fiber-glass [1]. Characteristics of the USP can be tuned by proper choice of the diacid or diol components in the esterification formulations. In most formulations, the principal diol, propylene glycol is partially replaced with diethylene glycol to impart cracking resistivity. To enhance thermal endurance and chemical resistance, isophthalic acid is preferred as the acid component.

In the commercial polyesterification processes, well-known acid catalysts such as H₂SO₄ and p-toluene sulfonic acid (PTSA) have been replaced with antimony and titanium based catalysts, to avoid their dehydrating effects yielding coloration. Titanium- and tin-containing catalyst systems show high efficiency, but may cause to coloration of the polyester product in longer reaction periods [2]. Although germanium metal powder has been demonstrated to reduce formation of cyclic oligomers [3]

and yield polyesters with high clarities, relatively high cost of the germanium metal deters its extensive use. One important aspect of the polyesterification with maleic anhydride is maleate–fumarate isomerization, which is useful to accelerate hardening with styrene. Such isomerization occurs at 220 °C and facilitated by using catalysts, such as piperidine and morpholine [4].

In the present work, boric acid is presented as a mild and convenient catalyst for preparing colorless USPs in relatively short reaction times using maleic anhydride as precursor for the unsaturated segments. The catalytic effect of boric acid was studied for polycondensation of the hydroxyethyl esters generated from cyclic anhydrides; namely maleic, succinic and phthalic anhydrides in various time-temperature conditions. This procedure was also employed for preparing unsaturated copolyesters using appropriate maleate–succinate and maleate–phthalate combinations. The resulting unsaturated polyesters were sulfonated by action of sodium hydrogen sulphite to give amphiphilic polyesters with interesting solution behaviors. To our best, there appear no reports in the literature, dealing with sulfonation of USPs and this paper would be the first report on the subject.

In the study, conditions of the polyesterification, maleate–fumarate isomerization and the sulfonation yields were discussed based on ¹H NMR, FT-IR spectra, and GPC and chemical analyses. The surfactant behaviors of the sulfonated polymers were investigated by surface tension, UV analyses.

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2. Experimental

2.1. Materials and methods

Boric acid (E. Merck), Phthalic anhydride (PHA) (E. Merck), maleic anhydride (MA) (Aldrich), succinic anhydride (SA) (Aldrich) and pyridine (Fluka) were used without any further purification.

¹H NMR spectra of the polymers were obtained by a Bruker 250 MHz NMR spectrometer, using CDCl₃ and D₂O as solvent for the polyesters and their sulfonated derivatives respectively. FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer. UV spectra and transparencies were obtained using Shimadzu UV 1240 model spectrometer. Gel Permeation Chromatography (GPC) traces of the polyester samples were taken in tetrahydrofuran (THF) with a flow rate of 0.3 mL/min using Agilent 1100 series instrument consisting of a pump, a refractive index-detector and Waters Styrogel (HR4, HR3, HR2) columns. Polystyrene was used as standard. Critical micelle concentrations (CMC) of the sulfonated polymers solutions were assigned by Young/Laplace surface tension method using KSV's CAM 200 surface tensionmeter, at 20 °C. The micelle sizes and size distributions in the sulfonated polymer solutions were determined by dynamical light scattering (DLS) method, using a Brookhaven 90 Zeta Plus Particle Sizing Instrument. Shapes and sizes of the micelles were assigned by Environmental scanning electron microscopy (ESEM) technique, using Philips – FEI XL30, ESEM-FEG instrument operating at 5.00 kV in STEM mode. In these measurements concentrations of aqueous polymer solutions were chosen slightly higher than their CMCs (4.2 and 3.1 gL⁻¹ for the sulfonated polyesters with 50% and 70% SA contents respectively).

2.2. Polyesterification of monohydroxyethyl esters of diacids using boric acid catalyst

The polyesterifications of ethylene glycol (diol component) with cyclic anhydrides were carried out in two steps. The reactions were performed in a single reaction vessel in which monohydroxyethyl esters of the diacids were formed first, by action of monoethylene glycol on the cyclic anhydrides; MA, SA and PHA. The ω-hydroxy acids generated were then, polycondensed in the presence of boric acid-pyridine mixture, in the second step. A typical procedure is as follows: To a 250 mL volume of flat bottom flask, there was added 18.6 g (0.3 mol) monoethylene glycol, 29.4 g (0.3 mol) MA and 50 mL toluene. The flask was equipped with a Dean–Stark trap and a reflux condenser and heated to 100 °C for 30 min to form monoester of maleic acid. To the cooled solution there was added 0.5 g H₃BO₃ and 5 mL pyridine and the mixture was heated at 130 °C and kept constant at this temperature until water evolution was ceased (ca. 4 h). Then, toluene was distilled off and the reaction mixture was poured into 200 mL of cold NaHCO₃ solution (3%). The silky white polymer was separated by decanting the water phase. The polymer was dissolved in 2-methoxyethanol (30 mL) and reprecipitated in 200 mL NaCl solution (10%). White polymer was dried at 50 °C for 24 h under vacuum. The yield was 38 g (89.1%).

The same procedure was employed to produce the polyesters and copolyesters constituting with succinate and phthalate segments.

2.3. Determination of the carboxyl end groups

One gram of the polyester sample was dissolved in 10 mL 2-methoxyethanol. To this solution, there was added 5 mL of ethanolic KOH solution (0.103 M). The mixture was shaken and poured into 35 mL of distilled water. The polyester precipitated was filtered and 40 mL of the filtrate was titrated with 0.1 M HCl

solution. The carboxyl end group content (in terms of mmol per gram) was calculated from;

$$a = 5 \times 0.103 - 0.1x/0.8$$

Where, x is the titer in mL.

2.4. Sulfonation of the unsaturated polyesters with sodium bisulfite

The USP sample (2 g) was dissolved in ethylene glycol monomethyl ether (15 mL). This solution was mixed with 15 mL NaHSO₃ solution (15%) and heated at 70 °C in a 100 mL volume of flask under reflux condenser. The mixture turned to be clear solution within 2 h. The reaction was continued for 24 h. The resulting solution was evaporated to dryness and the residue was dissolved in 15 mL ethylene glycol monomethyl ether and filtered. The sulfonated polymer was precipitated in 50 mL petroleum ether, filtered and dried under a vacuum (50 °C for 24 h). The resulting polymers were soluble in water, ethanol and DMF. Extents of the sulfonation reactions were assigned by ¹H NMR spectra of the polymers in D₂O.

3. Results and discussion

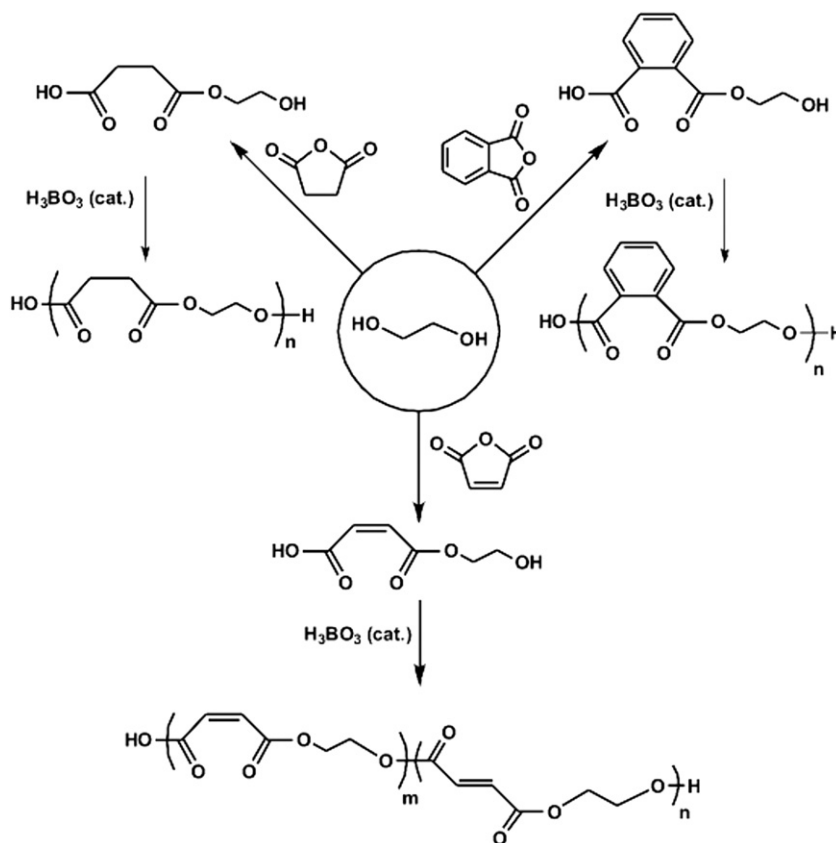
3.1. Polyesterification using boric acid as mild catalyst

The catalytic effect of boric acid was studied in polycondensation of hydroxy carboxylic acids in situ-generated by action of ethylene glycol on maleic, succinic and phthalic anhydrides. The reactions were carried out in one-pot using a typical polyesterification set up in which extents of the polycondensations were followed simply by monitoring volume of the water azeotropically removed with toluene at 130 °C. The reaction with catalytic amounts of boric acid, however, was very slow at this temperature. The esterification yield of the succinic acid semiester was around 70% within 8 h as inferred from volume of the evolved water.

Experiments showed that, addition of few milliliters of pyridine accelerates the reaction considerably, so that polyesterification is completed within 4 h at 130 °C. Therefore, the reactions were conducted in the presence of pyridine as cocatalyst. Overall scheme of the polyesterification is in situ generation of hydroxy carboxylic acids and their polycondensation using a boric acid-pyridine catalyst as depicted in Scheme 1.

Catalytic effect of boric acid must be due to easy formation of boron ester with the hydroxy groups of semi-esters of the dibasic acids. The boron ester intermediate undergoes to acidolysis with the free carboxyl group to form polyester. This acidolysis reaction is very slow in the absence of pyridine. Role of the pyridine is to dissociate the carboxyl group in the organic medium and proton of the pyridinium cation attacks to the boron-oxygen bond to generate carbocation on the alkyl fragment. Therefore, pyridine seems to be essential cocatalyst to speed up of the polyesterification. Similar ionizing effect of pyridine on carboxylic acids has been observed in direct esterification with alcohols [5]. The same effect of pyridine is likely to occur in acidolysis of alkyl borates. Simplified catalysis mechanism of the boric acid-pyridine couple is depicted in Scheme 2.

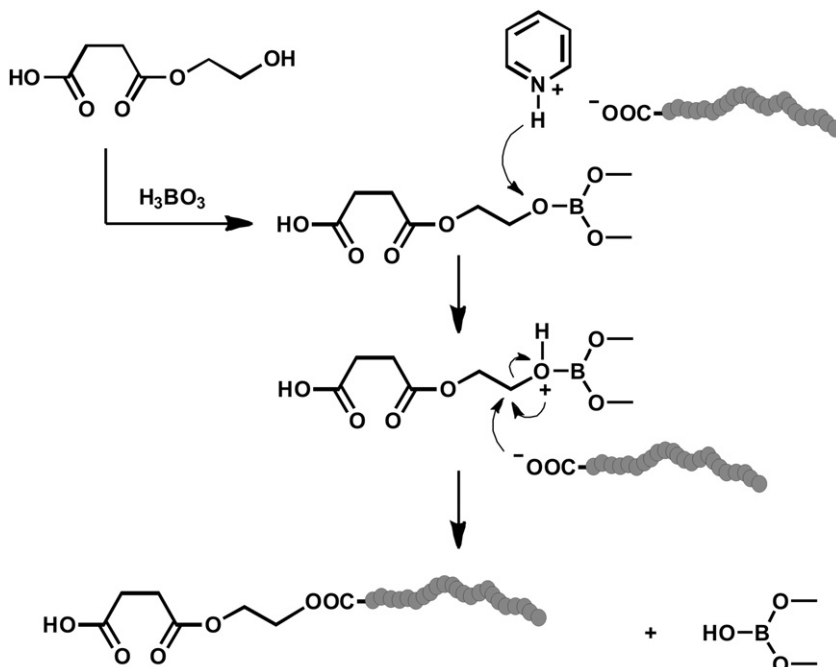
In order to prove this assumption, we carried out additional experiment in which tributyl borate was reacted with an equivalent amount of propanoic acid at 130 °C for 8 h. The reaction mixture was shaken with sodium carbonate solution and the organic layer constituting with butyl propionate and butanol was separated. Extent of the esterification was estimated by ¹H NMR spectrum of the mixture. An integral ratio of the CH₂–O proton signal of the



Scheme 1. Polyesterification of the monohydroxyethyl esters of maleic, succinic and phthalic acids with boric acid as mild catalyst.

ester at 3.8 ppm to that of CH_2-OH group signal of butanol at 3.5 ppm, revealed only 13% conversion. The repeated reaction in the presence of pyridine yielded nearly quantitative conversion, implying the deprotonating effect of pyridine.

The polycondensation of 2-hydroxyethyl esters derived from maleic, succinic and phthalic anhydrides in the presence of a boric acid-pyridine catalyst yielded colorless polyesters in low molecular weights (M_n : 1650–1950) within 4 h (Table 1) as inferred from the



Scheme 2. Possible mechanism of boric acid-pyridine catalysis in the esterification with carboxylic acids.

Table 1
Characteristics of the polymers obtained by polycondensation of ω -hydroxy carboxylic acids using boric acid catalyst.

ω -Hydroxy acid ^a	Polyester	React. time	Yield ^b (%)	Molecular weight ^c		-COOH end group content ^d (mmol g ⁻¹)
				M _n	M _w	
HES	Poly(ethylene succinate)	4 h	91.0	1800	2750	1.09 ± 0.02
HEP	Poly(ethylene phthalate)	4 h	92.2	1950	2950	ND
HEM	Poly(ethylene maleate-co-ethylene fumarate)	4 h	89.1	1650	2800	1.11 ± 0.02
HES + HEM (1:1)	Poly(ethylene succinate-co-ethylene maleate-co-ethylene fumarate)	4 h	88.7	1750	2400	1.06 ± 0.02
HEM + HEP (1:1)	Poly(ethylene phthalate-co-ethylene maleate-co-ethylene fumarate)	4 h	93.7	1950	3100	ND

^a The abbreviations; HES: 2-hydroxyethyl succinate, HEP: 2-hydroxyethyl phthalate, HEM: 2-hydroxyethyl maleate.

^b Practical yields.

^c By GPC.

^d ND: Not determined.

GPC traces. Extension of the reaction periods, however, did not change the molecular weights. This was attributed to slight change in alcohol to carboxylic acid ratio by evaporation traces amounts of ethylene glycol during the process at 130 °C.

Determination of the end groups of the polymers by titration revealed 1.06–1.11 mmol g⁻¹ of carboxylic acids, which are almost double comparing with the theoretical values. By assuming the presence of one carboxyl unit per chain, an average 1650 Da of molecular weight corresponds to 0.6 mmol carboxyl end group per gram of the maleate polyester. Comparing with 1.20 mmol of theoretical carboxyl content, 1.11 mmol g⁻¹ found for the polyester derived from MA implies that almost 90% of the polyester chains bear carboxyl groups in both ends. The remaining 10% carries one carboxyl end group per chain. The end group titration of the other polyesters gave similar results as given in Table 1. Those results confirm the assumption of ethylene glycol loss, which is responsible for the low molecular weights in the polycondensation process. This was also proven by a separate experiment in which the polycondensation with SA was repeated by using less volatile diethylene glycol as diol component. The number average molecular weight attained at the same period (4 h) was 4600.

Since molecular weights of the polyester are in desired ranges well suited with the classical hardening formulations, we did not attempt to increase the molecular weights any further. Apparently, the boric acid-pyridine acts as a mild catalyst for preparing colorless polyesters within short times, which are advantages of this catalyst system over the conventional esterification catalysts. Avoidance of the color formation in this process must be due to high thermal decomposition temperatures of the boron esters (>300 °C) [6].

¹H NMR spectra of the polymers confirm the polyester structures. Thus, in the ¹H NMR spectrum of the polymer (see supplementary data) obtained from succinic anhydride; the singlet at 4.3 ppm in is associated with CH₂ protons of the ethylene bridge. The protons of succinic acid component represent another singlet at 2.7 ppm. A similar pattern is observed for the case of poly(ethylene phthalate) (see supplementary data). In this spectrum, typical aromatic proton signals appear in 7.3–7.8 ppm and the multiplet centered at 4.3 ppm is due to protons of the ethylene bridge. The weak signal at 3.8 ppm is due to CH₂OH end groups of this polymer. An integral ratio of the last two peaks is around 1/18, which is consistent with the molecular weight of the polymer (M_n: 1950). Although such a consistency of GPC data with NMR is somewhat unexpected for the polyesters, this might be due to low molecular weight of the polymer.

¹H NMR spectrum of the polyester derived from maleic anhydride (Fig. 1) exhibits two different proton signals associated with

the maleate and fumarate double bonds at 6.4 and 6.9 ppm respectively. Integral ratio of the two peaks implies about 80% of fumarate segment in the polymer.

Two weak signals at 5.85–6.15 ppm (labeled by asterisks) represent protons of =CH–COO moieties associated with maleic and fumaric acid end groups. Since optimal temperature of maleate–fumarate isomerization is 200 °C, eighty percent of the isomerization seems to be reasonably high at this temperature. However, considering with accelerating effect of amines such as piperidine and morpholine [7], this isomerization is not unexpected and might happen by action of pyridine present in the reaction medium. As a result polymerization of 2-hydroxyethyl maleate yields fumarate rich (80%) unsaturated polyester, poly(ethylene maleate-co-ethylene fumarate), in the conditions studied.

3.2. Sulfonation of the polyesters

In this part of the work, addition of sodium hydrogen sulphite to ethylenic double bonds of the unsaturated polyesters was studied. The reaction with slightly excess of sodium hydrogen sulphite in 2-methoxyethanol–water mixture resulted in quantitative sulfonation of the maleate and fumarate double bonds (Scheme 3).

Chemistry of bisulfite addition to ethylenic double bonds is well documented in the literature [8]. The bisulfite addition to mono and dialkyl esters of maleic acid is common method to produce

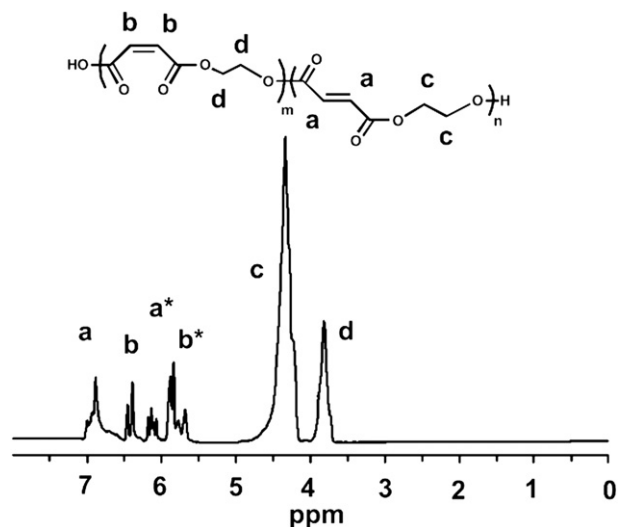
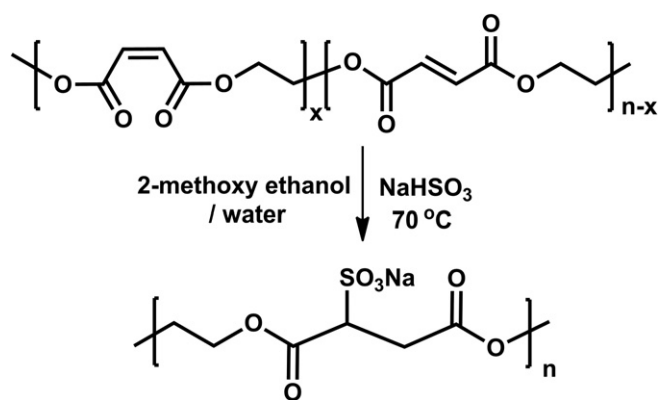


Fig. 1. ¹H NMR spectrum of the polymer, poly(ethylene maleate)₂-co-poly(ethylene fumarate)₉ (M_n:1650) obtained by boric acid catalyzed polycondensation of 2-hydroxyethyl maleate in the presence of pyridine.



Scheme 3. Sulfonation of the unsaturated polyester, poly (ethylene maleate/fumarate).

corresponding sulfonate derivatives, e.g., dioctyl sulfosuccinate (also known as Aerosil OT or AOT) having extensive use in textile industry and in paint formulations [9].

However, sulfonate derivatives of polymeric maleates have not been reported so far. Synthesis of sulfonated polyesters was considered to be interesting due to degradable nature of the polymer backbone and possible “Gemini surfactant” effect of the multiple sulfonate groups. Sulfonation of the USP in this work was carried out with sodium hydrogen sulphite in 2-methoxyethanol–water mixture (1:1). The polyesters derived from MA, MA–SA (1/1 mol/mol) and MA–SA (3/7 mol/mol) mixtures were sulfonated by this procedure. Sulfonation of the maleate–phthalate copolyester was not studied, owing to its hydrolytic instability in aqueous medium [10]. Interestingly, the sulfonated polyesters are soluble in broad range of polar organic solvents including water, DMF and NMP or in their mixtures depending on the succinate content.

Those solution behaviors revealed potential use of these materials as emulsifying, stabilizing or solubilizing agents in *o/w* or *w/o* systems.

^1H NMR spectrum of the sulfonation product obtained by bisulfite addition of poly (ethylene maleate/fumarate) is given as a representative example in Fig. 2. It is clearly seen that proton signals of maleate and fumarate double bonds at 6.4 and 6.9 ppm disappear completely after the bisulfite addition. This result indicates quantitative sulfonation of maleate and fumarate double bonds at this temperature. Protons of the ethylene bridge in the sulfonated polymer exhibit two separate peaks at 4.3 and 3.8 ppm for the CH_2 groups. New peaks emerging in 3.6–3.3 ppm range are due to CH and CH_2 protons of the sulfosuccinate segments.

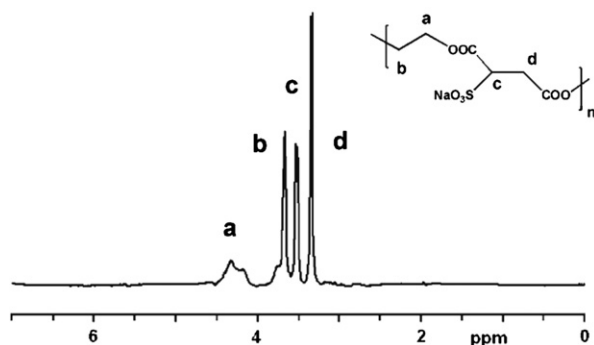


Fig. 2. ^1H NMR spectrum of the sulfonated polyester derived from 2-hydroxyethyl maleate (in D_2O).

Similar pattern is observed in ^1H NMR spectrum of the sulfonated maleate–succinate copolyester (see supplementary data) in which the signals above 5 ppm disappear and typical proton signals of succinate group appear in 2.4–2.7 ppm range.

Sulfonation of the polyester derived from MA is also evidenced by FT-IR spectra (see supplementary data). Thus, characteristic carbonyl band and C=C stretching vibration band of the maleate and fumarate segments appears at 1720 cm^{-1} and at 1650 cm^{-1} respectively. In the FT-IR spectrum of the sulfonated product the carbonyl band slightly shifts to 1730 cm^{-1} . Disappearance of the double bond vibration at 1650 cm^{-1} is not clearly observable due to new carbonyl band emerged in the same region, $1630\text{--}1650\text{ cm}^{-1}$. This band is present also in the FT-IR spectrum of commercial dioctyl sulfosuccinate (AOT) [11] that is a low molecular weight analogue of the sulfonated polymer and can be attributed to stretching vibration of the carbonyl group adjacent to the sulfonate group. Lower frequency of this band must be due to increased enolization behavior of C=O group. This polymer displays also asymmetric vibration band of S=O at 1180 cm^{-1} and a broad O–H stretching vibration band around 3300 cm^{-1} .

To examine surfactant behavior of the sulfonated polymer samples, their critical micelle concentrations (CMC) were measured by surface tension method. Fig. 3 shows surface tensions of the polymer surfactants as a function of concentration. It is seen that, the sulfonated polymer with 50% SA content exhibits significant change in surface tension around 3.4 g per liter concentration which is assigned to its CMC (Table 2). Similar estimation for the polymer with 70% SA gives a CMC of about 2.9 g per liter.

Micelle forming behaviors of the sulfonated polyesters were investigated by DLS and ESEM techniques. In these experiments, the polymer concentrations were chosen slightly higher than those of their CMC's (4.2 and 3.1 gL^{-1} for 50% and 70% SA contents respectively). DLS trace of the polymer with 50% SA content (Fig. 4) shows an average particle diameter of 194.5 nm and relatively low polydispersity (0.323) as inferred from the relevant histogram (Fig. 4). ESEM image of this solution (Fig. 5) represents spherical micelles with nearly equal sizes. These results are in good agreement with DLS data.

Significantly, larger average particle size (538.6 nm) and a wider polydispersity (0.343) are observed in DLS picture of the polyester with 70% SA content (Fig. 6a and b).

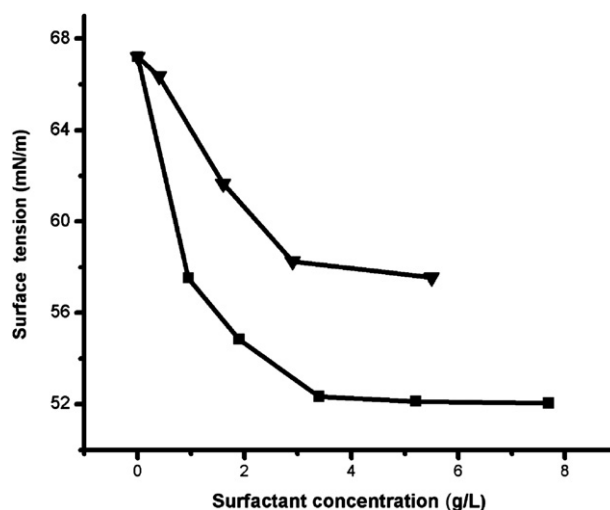


Fig. 3. Surface tension–surfactant concentration plot for the sulfonated polymer with 50% SA content (■), with 70% SA content (▼).

Table 2
Structural and solution characteristics of the sulfonated polyesters.

Unsaturated polyester	Succinate Content mol %	Sulfonation Degree ^a	CMC ^b (g/L)	Average ^c Micelle size	Solubility
Poly(ethylene maleate-co-ethylene fumarate)	—	100%	—	—	Water, DMF, DMSO
Poly(ethylene succinate-co-ethylene maleate-co-ethylene fumarate)	50%	100%	3.4	194.9 nm	Water-acetone (1:1), Water-THF (1:1)
Poly(ethylene succinate-co-ethylene maleate-co-ethylene fumarate)	70%	100%	2.9	538.6 nm	Water-DMF(1:1) DMSO

^a Based on ¹H NMR spectra.

^b Critical Micelle Concentration by surface tension Measurements.

^c By DLS.

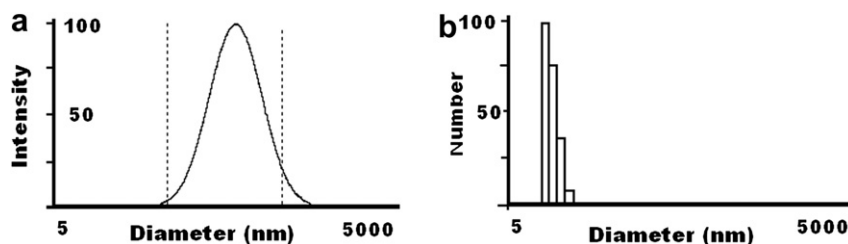


Fig. 4. DLS trace of the aqueous solution of the sulfonated polymer with 50% SA (a) and histogram of its hydrodynamic diameter (b) (Concentration: 4.2 gL⁻¹).

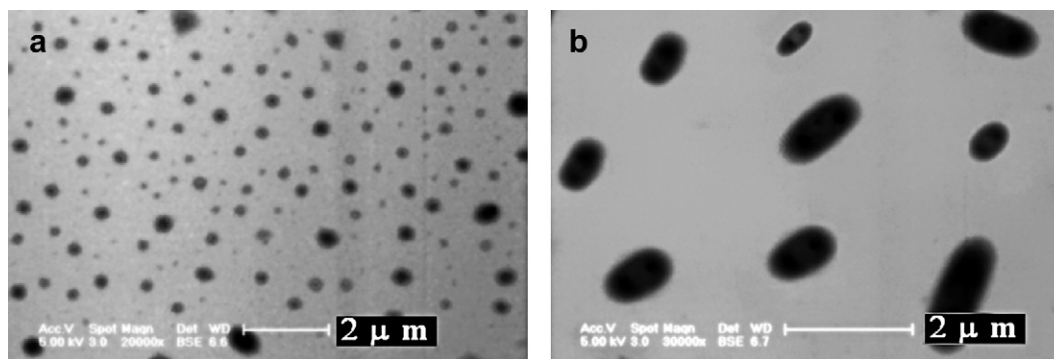


Fig. 5. Representative ESEM micrographs of the micelles taken in the solution of sulfonated polymer with 50% SA content (4.2 gL⁻¹) (a) and with 70% SA content (3.1 gL⁻¹) (b). The images were taken by the samples drop cast from aqueous solutions, without staining.

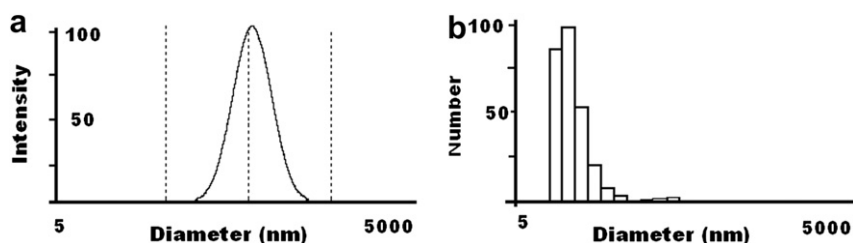


Fig. 6. DLS trace of the aqueous solution of the sulfonated polymer with 70% SA (a) and histogram of its hydrodynamic diameter (b) (Concentration: 3.1 gL⁻¹).

Apparently, increasing SA content of the polymer from 50% to 70% increases the average micelle diameter by a factor of 2.5, in accordance with its greater hydrophobicity. However, mostly ellipsoidal micelles are seen in the ESEM image of this solution (Fig. 5). Overall results of DLS and ESEM measurements imply amphiphilicity and micellar behavior of the sulfonated polymer samples.

It is important to note that, sulfonated derivative of the polyester constituting only with maleate segments was hydrophilic and its aqueous solution did not show any sign of micelle formation.

4. Conclusion

Polyesterification of the hydroxy carboxylic acids, in situ-generated from cyclic anhydrides, MA and SA proceeds with a boric acid-pyridine catalyst to give colorless oligoesters. Comparing with 8–25 h of reaction periods for the conventional polyesterification process, short reaction time of the process (4 h) is helpful to avoid coloration and to suppress branching or cross-linking via addition of the hydroxy groups to maleate double bonds

as a side reaction. The USPs easily adds sodium bisulfite to give sulfonated derivatives having good solubilities in many solvents. Since the maleate ratio of the copolyester is adjustable parameter, this procedure allows preparing degradable polymer surfactants with desired hydrophilicities.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.polymer.2010.08.066](https://doi.org/10.1016/j.polymer.2010.08.066).

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