Solubility behavior of amphiphilic sulfonated copolymers based on styrene–stearyl methacrylate and styrene–stearyl cinnamate

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ABSTRACT: Amphiphilic polymers have found many applications, so many types of these copolymers have been prepared. Specifically, sulfonated polystyrene acts, for example, as a flocullant or dispersant of petroleum asphaltenes as a function of its hydrophilic–hydrophobic balance. However, when changing the sulfonation degree, looking for the best performance, the solubility also changes, and sometimes it is responsible for making the polymer unsuitable for any application. Therefor, this work investigates in detail the changes in the solubility range of copolymers based on styrene–stearyl methacrylate and styrene–stearyl cinnamate with different molar compositions and different sulfonation degrees. The copolymers were synthesized and characterized by ^{1}H-NMR, Fourier transform infrared spectroscopy, and elemental analysis. In the range of compositions analyzed, with increasing content of long hydrocarbon chains, not only the displacement of the solubility in solvents with lower solubility parameter (δ), but also the broadening of the solubility range was observed. In general, the solubility was directly related to the sulfonic group content, but there appeared to be an influence of the randomness of the sulfonation reactions along the chains. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43112.

INTRODUCTION

Amphiphilic polymers have widespread applications. In the petroleum industry, they are used in drilling fluids[1–4] and for demulsification of water-in-oil emulsions,[5] inhibition of wax deposition,[6–12] stabilization of asphaltenes in crude oil,[13–16] flocculation of asphaltenes,[17–19] inhibition of naphthenate deposition,[20] enhanced oil recovery,[21–23] and water treatment.[24,25] In drilling, hydrophobically modified starches can be used to control filtrate from emulsified fluids.[26,27] For demulsification of emulsions, the great majority of demulsifier agents are based on surfactant copolymers of poly(propylene oxide)–poly(ethylene oxide).[5] Copolymers made from ethylene and vinyl acetate and acrylic copolymers with long hydrocarbon chains have long been used to inhibit deposition of paraffins from crude oil.[7,9,12] Polymers containing cardanol and sulfonated polystyrene have been tested as stabilizers/flocculants of asphaltenes in petroleum.[17–19] Each specific application requires distinct chemical structures and molar masses.

The development of copolymers based on stearyl methacrylate with amphiphilic properties has been reported in the literature.[26–33] Stearyl methacrylate is considered a versatile monomer because its pendant group in the polymer structure provides self-assembly properties.[34] Styrene-*b*-stearyl methacrylate copolymers can self-organize[35] as aggregates in the presence of organic solvents[36] and would be tested as an asphaltene stabilizer. Amphiphilic copolymers containing ionic groups have been divided in two classes according to their dissociation behavior: weak acid/base and strong acid/base. The synthesis of polyelectrolytes containing in their structure strong acid groups has not been extensively reported, and this could be related to the difficulty in synthesizing them due to the large differences between (1) the hydrophilicity and hydrophobicity of the segments and (2) the monomer solubility.[37] Chemical modification of the polymer chain is an alternative to obtain copolymers containing strong acid groups,[38] for example, by inserting sulfonic
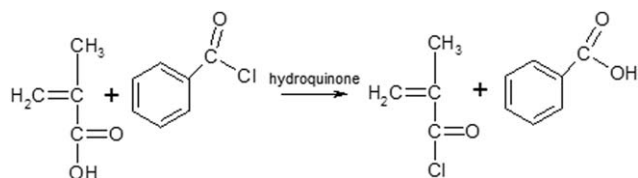
Figure 1. Synthesis of methacryloyl chloride.

Figure 3. Synthesis of cinnamoyl choride.

groups following homogeneous or heterogeneous methods.[30–40] The suitability of each method is related to the desired sulfonation degree and to the reaction yield. Several kinds of sulfonation agents have been used, such as sulfanilic acid[41]; sulfur trioxide; sulfuric acid[42]; chlorosulfonic acid; lauryl, stearyl, or acetyl sulfate; and complexes of sulfur trioxide with alkyl phosphates and dioxane.[39]

Besides the chemical structure of the polymer, its solubility behavior in the medium also plays an important role in the performance in each application.[10,43] Therefore, controlling the solubility of amphiphilic polymers is fundamental for the proper structure–performance relation of molecules with specific applications. However, the solubility behavior has not been investigated in detail as a function of variations in the hydrophilic–lypophilic relation of molecules. This article describes the synthesis and characterization of a family of amphiphilic molecules and assesses the variation of their solubility performance in solvents with different solubility parameters as a function of the resulting amphiphilic structure, describing the range of solubility parameters in which the copolymers are soluble.

EXPERIMENTAL

Synthesis and Characterization of Copolymers

To obtain the copolymers, methacryloyl chloride and cinnamoyl chloride were synthesized first, followed by the synthesis of monomers of stearyl methacrylate and stearyl cinnamate.

Reagents. Cinnamic acid 99.0% (recrystallized with ethyl acetate), styrene spectrum grade (distilled under vacuum), and toluene (distilled at 110 °C and dried with aluminum oxide) were supplied by Vetec Química Fina, Xerém, Brazil. Acetic anhydride 99.5%, benzoyl chloride P.A., dichloromethane 99.5%, 1,4-dioxane P.A., ethyl alcohol 95.54 °GL, n-heptane 99.5%, n-hexane 99.5%, hydroquinone P.A., isopropyl alcohol 99%, methacrylic acid 90.0%, pyridine P.A., sulfuric acid P.A., thionyl chloride 99.0%, and triethylamine P.S. were also supplied by Vetec Química Fina, Xerem, Brazil, and used as received. Stearyl alcohol P.S. (recrystallized with n-hexane) were supplied by Merck, São Paulo, Brazil. Deuterated chloroform was supplied by Cambridge Isotopic Laboratory, São Paulo, Brazil. Tetrahydrofuran HPLC/ spectro was supplied by Tedia Brasil, São Paulo, Brazil.
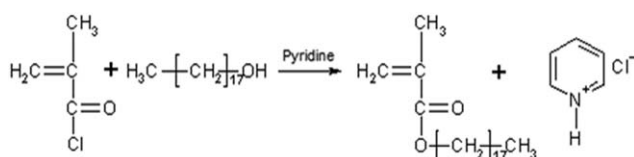
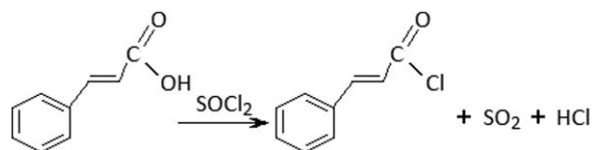**Synthesis of the Monomer of Stearyl Methacrylate.** First, the methacryloyl chloride (Figure 1) was synthesized in a three-neck balloon flask by reacting methacrylic acid and benzoyl chloride at a molar ratio of 1:1.4 in the presence of 10% hydroquinone, according to the method described by [13]. The product was bidistilled between the temperatures of 98 and 100 °C and kept in an amber flask in a refrigerator.

To obtain the stearyl methacrylate (Figure 2), methacryloyl chloride (0.027 mol) and stearyl alcohol (0.1 mol) were reacted in toluene in the presence of pyridine (0.03 mol). First the methacryloyl chloride was added dropwise into the reaction mixture at a temperature of 10 °C. After the formation of the white precipitate of pyridinium chloride, the reaction mixture was left at rest until reaching room temperature and then was submitted to reflux at 70 °C for 2 h. The product was vacuum-filtered under an inert nitrogen flow for 24 h in order to remove the pyridinium chloride from solution, and then the liquid obtained was rotary-evaporated at 100 °C to remove the toluene and isolate the monomer.

Synthesis of the Monomer of Stearyl Cinnamate. Cinnamoyl chloride was used as the precursor to synthesize stearyl cinnamate ester. The cinnamoyl chloride was obtained from reacting (Figure 3) cinnamic acid (0.3 mol) with thionyl chloride (0.3 mol) under reflux at 50 °C for 1 h, and then at 80 °C for another 2 h.[44] After cooling to room temperature, triethylamine (TEA) (0.3 mol) was added to the cinnamoyl chloride (0.3 mol), followed by stearyl alcohol (0.3 mol), at a temperature of 0 °C. At the end of this addition, the system temperature was raised to 80 °C, and it was left under reflux for 2 h. After crystallization in hexane, the stearyl cinnamate (Figure 4) was stored in an amber flask.

Synthesis of the Copolymers of Styrene–Stearyl Methacrylate (SSMA). The copolymerization reactions were conducted in mass (SSMAmass) and in solution (SSMAsol), with benzoyl peroxide (BPO) as initiator at 80 °C under an inert nitrogen atmosphere. The copolymers were synthesized with different molar ratios between the monomers styrene (STY) and stearyl methacrylate (SMA) (50/50, 70/30, 95/5) and different reaction times. For the solution reaction, toluene was used as a solvent at 0.5 mL of monomer per mL of solvent. After the end of the reaction, the polymer obtained by mass polymerization was solubilized in dry toluene. All samples were precipitated in chilled ethanol. The polymer was then recovered by vacuum filtration and heated in an oven at 40 °C for complete drying.
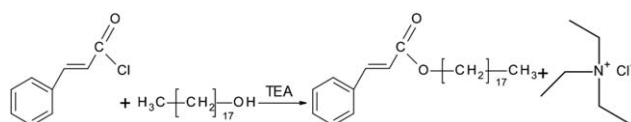

Figure 2. Synthesis of stearyl methacrylate.

Figure 4. Synthesis of stearyl cinnamate.

Synthesis of the Copolymers of Styrene–Stearyl Cinnamate (SSC). The copolymerization reactions of styrene with stearyl cinnamate were conducted in mass (SSCmass) with benzoyl peroxide (BPO) as initiator at 80 °C under an inert nitrogen atmosphere. The copolymers were synthesized with different molar ratios between the monomers styrene (STY) and stearyl cinnamate (CIN) (70/30 and 95/5) and different reaction times. At the end of the reaction, the polymer was solubilized in dry toluene and precipitated in chilled ethanol. The polymer was then recovered by vacuum filtration and heated in an oven at 40 °C for complete drying.

Sulfonation of Copolymers. The copolymers of SSMA and SSC were submitted to sulfonation with acetyl sulfate according to the methods described in the literature.[45,46] First, the polymer was dissolved in dichloromethane (10% m/v) at the solvent reflux temperature (40 °C) for 30 min. Next, a solution of acetyl sulfate was added, which had been previously prepared from a mixture of acetic anhydride (1.12 mL), dichloromethane (1.00 mL), and sulfuric acid (0.37 mL) in an ice bath. The appearance of a yellowish color was taken as indication of the sulfonation reaction, which was maintained under constant stirring for different intervals (15, 30, 60, 90, or 120 min). After the preestablished time, 5 mL of isopropyl alcohol was added, and the system was maintained under stirring for another 30 min. The sulfonated copolymer was recovered by precipitation in distilled water followed by freeze-drying (Liotop K105 freeze dryer), washed in distilled water, and dried in an oven at 40 °C.

Characterization of Monomers and Polymers
The monomers were characterized by NMR and the copolymers by NMR, Fourier transform infrared spectroscopy (FTIR), and size exclusion chromatography (SEC). The sulfonated copolymers were characterized by FTIR and elemental analysis.

^{1}H Nuclear Magnetic Resonance. The monomer and polymer samples were dissolved in deuterated chloroform and analyzed in a Varian Mercury 300 ^{1}H-NMR spectrometer (Palo Alto, California) with frequency of 300 MHz, utilizing tetramethylsilane (TMS) as internal reference. A 5 mm tube was used, and the sample concentration was approximately 0.1 wt/v %. The data were treated with the MestRe-C software (Santiago de Compostela, Spain).

To determine the composition of the SSMA copolymers, we used the areas related to the methyl hydrogens of the terminal methyl group (CH$_3$) of the hydrocarbon segment of the stearyl methacrylate, which presents a chemical shift at 0.89 ppm, and the aromatic hydrogens of the styrene segment, with chemical shift between 6.6 and 7.4 ppm. Equations (1) to (3) describe the calculations for measurement of the molar ratios of the STY-SMA (SSMA) copolymers:

$$\frac{N}{M} = \frac{5X}{3Y} \tag{1}$$

$$\%STY = \frac{\text{mol STY}}{\text{mol copolymerSSMA}} \times 100 \quad \text{or} \quad \%STY = \frac{X}{(X+Y)} \times 100 \tag{2}$$

$$\%SMA = \frac{\text{mol SMA}}{\text{mol copolymer}} \times 100 \quad \text{or} \quad \%SMA = \frac{Y}{(X+Y)} \times 100 \tag{3}$$

where N is the area under the peak referring to the aromatic hydrogens of styrene, M is the area under the peak referring to the hydrogens of the terminal methyl group of stearyl methacrylate, X is the hydrogens related to the aromatic ring; Y is the hydrogens related to the terminal methyl of stearyl methacrylate, %STY is the molar percentage of styrene present in the copolymer, and %SMA is the molar percentage of stearyl methacrylate present in the copolymer.

In turn, to determine the composition of the SSC copolymers, we used the areas corresponding to the methyl hydrogens of the terminal methyl group (CH$_3$) of the hydrocarbon segment of stearyl cinnamate, which presents a chemical shift at 0.90 ppm, and the hydrogens of styrene, with chemical shift between 6.2 and 7.25 ppm. Equations (4) to (6) describe the calculations to measure the molar ratios of the STY-CIN (SSC) copolymers:

$$\frac{A}{B} = \frac{5E + 5C}{3C} \tag{4}$$

$$\%STY = \frac{\text{mol STY}}{\text{mol copolymer SSC}} \times 100 \quad \text{or} \quad \%STY = \frac{X}{(X+Y)} \times 100 \tag{5}$$

$$\%CIN = \frac{\text{mol CIN}}{\text{mol copolymer SSC}} \times 100 \quad \text{or} \quad \%STY = \frac{Y}{(X+Y)} \times 100 \tag{6}$$

where A is the area under the peak referring to the aromatic hydrogens of styrene and stearyl cinnamate, B is the area under the peak referring to the hydrogens of the terminal methyl group of stearyl cinnamate, E is the hydrogens related to the aromatic ring of styrene; C is the hydrogens related to the terminal methyl group and the hydrogens of the aromatic ring of stearyl cinnamate, %STY is the molar percentage of the styrene present in the copolymer, and %CIN is the molar percentage of the stearyl cinnamate present in the copolymer.

Fourier Transform Infrared Spectroscopy. The sulfonated and nonsulfonated copolymers were characterized qualitatively by FTIR with an attenuated total reflectance (ATR) accessory. The spectra were acquired in the region between 4000 and 600 cm^{-1}, with resolution of 16 cm^{-1}. The analyses were performed with a Varian 3100 FTIR spectrometer with a germanium crystal ATR accessory.

Elemental Analysis. The content of the sulfonic groups present in the sulfonated copolymers of SSMA and SSC were determined with a LECO SC 632 sulfur analyzer (St. Joseph, Michigan). The elemental analysis technique involves burning the sample in a tubular oven at 1500 °C under oxygen flow. The sulfur is converted into SO$_2$ and oxidized to SO$_3$. Finally, the gases pass through an infrared detector, and the percentage by mass of sulfur (S) is calculated by the device by integration of the area under the SO$_3$ peak and by the sample mass. The sulfur content was determined by the device in mass percentage, and then the sulfonation degree was calculated by eq. (7), where DS is the degree of substitution of the sulfonic groups in the copolymer chain, "mass of mer" is the molar mass of the monomeric unit

Table I. Solubility Parameters of Solvents Used in Solubility Tests

| Solvents	Solubility parameter, δ (MPa$^{1/2}$)
n-Heptane	15.3
n-Heptane:dioxane 95:5	15.56
n-Heptane:dioxane 90:10	15.82
n-Heptane:dioxane 80:20	16.34
n-Heptane:dioxane 70:30	16.86
n-Heptane:THF 30:70	18.24
n-Heptane:dioxane 40:60	18.42
n-Heptane:THF 20:80	18.66
n-Heptane:dioxane 35:65	18.68
n-Heptane:THF 10:90	19.08
n-Heptane:dioxane 20:80	19.46
THF	19.5
Dioxane	20.5
Dioxane:isopropanol 90:10	20.8
Dioxane:isopropanol 70:30	21.4
Dioxane:isopropanol 50:50	22.0
Dioxane:isopropanol 30:70	22.6
Dioxane:isopropanol 20:80	22.9
Dioxane:isopropanol 10:90	23.2
Isopropyl alcohol	23.5

comprising styrene and stearyl methacrylate after the copolymerization, S is the mass percentage of sulfur, and 32 and 81 are the molar masses of sulfur and the sulfonic group, respectively.

$$DS = \frac{\text{mass of mer} \times 100 \times S}{32 \times 100 - (81 \times S)} \qquad (7)$$

Size Exclusion Chromatography. SEC enables obtaining a distribution profile of the molar masses and the relative values of the number-average molar mass ($\overline{M_n}$) and weighted-average molar mass ($\overline{M_w}$).[47] For that purpose, we used three KF-806M (Munich, Germany) chromatographic columns in series, covering a broad molar mass range. Tetrahydrofuran (THF) was used as the mobile phase, and the samples were prepared at a concentration of 0.5% (p/v) and filtered through a hydrophilic membrane (Durapore-Millipore (Darmstadt, Germany), 0.45 μm mesh) before injection in the columns. The equipment used was a Viscotek (Worcestershire, England) GPC Max VE-2001 multidetector.

Solubility Behavior of the Polymers
The SSMA and SSC copolymers, with and without sulfonation, were tested for solubility to correlate the solubility with the sulfonation degree resulting from the different reaction times for each copolymer. The solvents used in the solubility tests, as well as the respective solubility parameters,[48–50] are reported in Table I. The solubility parameter (δ) is such a guide to aid in predicting mutual solubility, and it is based on the principle that "like dissolves like." The term solubility parameter was first used by Hildebrand and Scott, and for solvents it can be calculated by the square root of the cohesive energy density.[48–50] The solubility tests involved mixing 2 mL of solvent and 10 mg of each
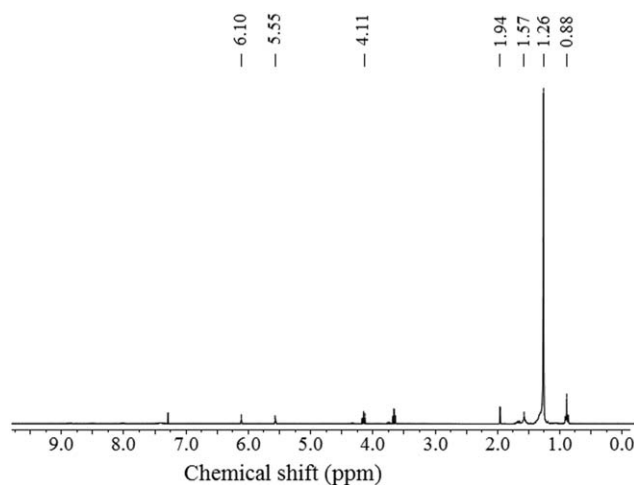
Figure 5. ^{1}H-NMR spectrum of stearyl methacrylate.

sample in a test tube. The tubes were closed with stoppers and kept at room temperature for 24 h for subsequent analysis of solubility of the samples in the solvents employed.

Some binary mixtures of these solvents were also prepared, and their solubility parameter values were calculated based on the weighted average (by volume fraction in the mixture) of the solubility parameters of the pure solvents, according to eq. (8):

$$\delta_{\text{mix}} = (\delta_1 \times \phi_1) + (\delta_2 \times \phi_2) + \ldots + (\delta_n \times \phi_n) \qquad (8)$$

where δ denotes the solubility parameter, and ϕ is the fraction by volume of each solvent in the mixture.

The solubility parameters of the solvent systems varied as a function of the type of solvent and the composition used, as shown also in Table I.

RESULTS AND DISCUSSION

Characterization of the Monomers and Copolymers by ^{1}H-NMR and SEC
The monomer stearyl methacrylate, prepared by reacting methacryloyl chloride and stearyl alcohol, was characterized by ^{1}H-NMR. The spectrum shown in Figure 5 presents peaks at 6.10
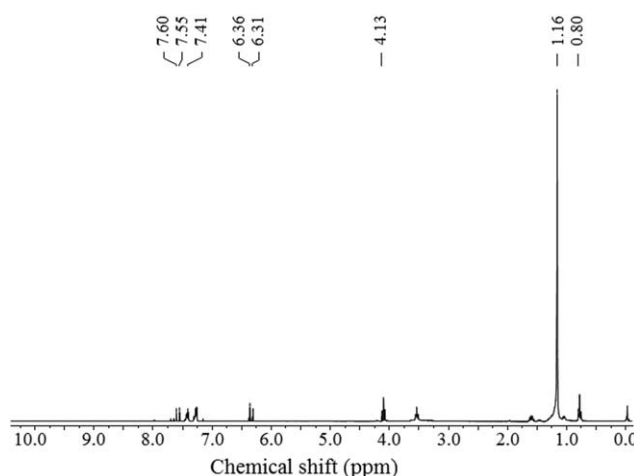
Figure 6. ^{1}H-NMR spectrum of stearyl cinnamate.
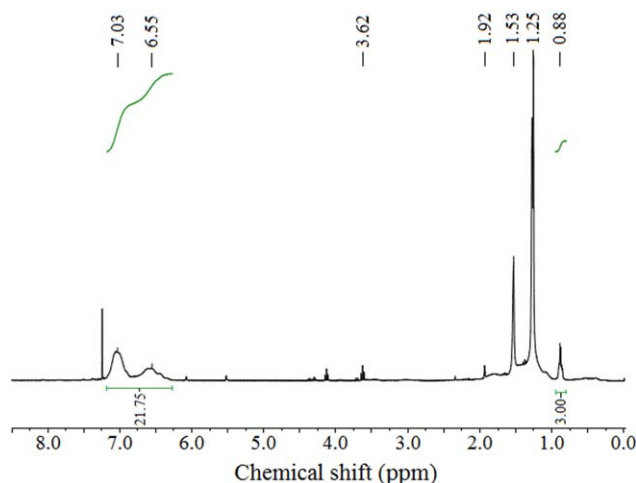
Figure 7. ^{1}H-NMR spectrum of SSMA copolymer (SSMA-mass2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. ^{1}H-NMR spectrum of SSC copolymer (SSC-mass2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and 5.55 ppm, referring to the hydrogens bound to the unsaturated carbon atom; a peak at 4.11 ppm related to the hydrogens bound to the carbons together with oxygen ($-O-CH_2-$) and characteristic of esters; a peak referring to the hydrogens of the methyl radical near the unsaturation, at 1.94 ppm; a stronger peak, with chemical shift at 1.26 ppm, related to the methylene hydrogens referring to the hydrocarbon segment of the stearyl radical; and a peak at 0.88 ppm, referring to the terminal methyl radical of the mentioned hydrocarbon radical.

The monomer stearyl cinnamate, obtained by reacting thionyl chloride with cinnamic acid, was also characterized by ^{1}H-NMR. The spectrum shown in Figure 6 presents peaks at around 7.29 and 7.5 ppm, related to the hydrogens of the aromatic ring of cinnamic acid; peaks at 6.30 ppm, referring to the hydrogens near the unsaturation; peaks at 4.13 ppm, related to the hydrogens linked to the carbon near the oxygen ($O-CH_2$) and characteristic of an ester group; a stronger peak, with chemical shift at 1.18 ppm, related to the methylene hydrogens referring to the hydrocarbon segment of the radical stearyl; and a peak at 0.90 ppm, referring to the terminal methyl radical of the mentioned hydrocarbon radical. These peaks appear in

regions of lower chemical shift because they are only weakly influenced by the chemical environment.

The ^{1}H-NMR spectra of the SSMA-mass2 and SSC-mass2 copolymers are presented in Figures 7 and 8, respectively.

The spectrum shown in Figure 7 confirms that the desired structure of the SSMA copolymer was achieved. This confirmation can be inferred from the disappearance of the characteristic hydrogen peaks of the unsaturation of both monomers, which normally appear at 5.22, 5.73, and 6.29 ppm for styrene and at 5.54 and 6.09 ppm for stearyl methacrylate. In the region related to the monomeric unit, traces of double bonds of residual monomers can be observed. Other peaks that corroborate the expected structure are found near 6.5 and 7.5 ppm, referring to the hydrogens of the aromatic rings, and in the region between 0.7 and 1.9 ppm, referring to the hydrocarbon segment of stearyl methacrylate.

Examination of the spectrum of SSC in Figure 8 shows a chemical shift, indicating the formation of the desired copolymer. This confirmation is related to the disappearance of the characteristic hydrogen peaks of the unsaturation of both monomers, which

Table II. Composition and Molar Mass of the Copolymers SSMA and SSC

Code	Molar composition at feed (STY/SMA)	Molar composition at feed (STY/CIN)	Molar composition by ^{1}H-NMR	Reaction time (h)	$\bar{M}_n$ (g/mol)	$\bar{M}_w/\bar{M}_n$
SSMA-mass1	95/5	-	95/5	1.5	126,000	2.84
SSMA-mass2	70/30	-	81/19	3	136,000	4.34
SSMA-mass3	70/30	-	82/18	4	56,500	2.42
SSMA-mass4	70/30	-	82/18	5	67,800	4.62
SSMA-mass5	50/50	-	53/47	5	92,300	2.87
SSMA-sol1	70/30	-	83/17	48	36,600	2.00
SSMA-sol2	50/50	-	60/40	48	123,000	2.10
SSC-mass1	-	95/5	93/7	1.5	63,600	2.30
SSC-mass2	-	70/30	85/15	6.5	72,400	1.80

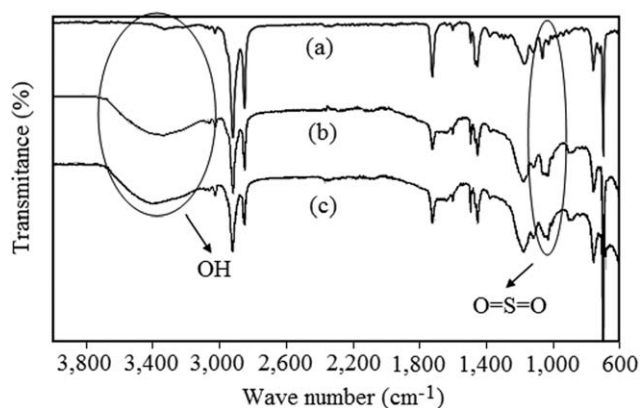**Figure 9.** FTIR spectra of SSMA copolymer with reaction time of 4 h (SSMA-mass4) and theoretical molar ratio of 70/30 (styrene/cinnamate): (a) before sulfonation, (b) after 15 min sulfonation, and (c) after 2 h sulfonation.

normally appear at 5.22 and 5.73 ppm for styrene and at around 6.30 ppm for stearyl cinnamate. Other peaks that corroborate this inference are found in the region between 6.20 and 7.25 ppm, related to the aromatic hydrogens of both monomers (styrene and stearyl cinnamate). The regions of low chemical shift contain the peaks referring to the hydrogens of the hydrocarbon segment of stearyl cinnamate, as well as the hydrogens of the methyl terminal, appearing in the region of 0.90 ppm.

^{1}H-NMR spectra were obtained for the other copolymers and all of them showed the same chemical shifts.

The molar mass composition values of the copolymers obtained by SEC and all of the reaction variables are reported in Table II. The molar composition results show that the concentration of styrene incorporated in both the SSMA chain and the SSC chain is greater than that of the feed. This result is related to the reactivity ratio of the monomers involved in each reaction.

Characterization of the Sulfonated Copolymers by FTIR

The sulfonated copolymers were characterized by FTIR. These analyses were performed on copolymer samples before sulfonation and after sulfonation at times of 15 min and 2 h. The FTIR spectrum of SSMA with monomer ratio of 70/30 (SSMA-mass4) is presented in Figure 9. The spectra of the sulfonated copolymers [Figure 9(b) and (c)] both contain a band in the region of 1030 cm^{-1}, characteristic of symmetric stretching of the O=S=O fragment present in the sulfonic group.[51] Another

vibration, indicating the presence of sulfonic groups in the copolymer after the reaction, is found in the region between 2900 and 3600 cm^{-1}. This wide band is characteristic of the stretching of the O—H bond related to the SO$_3$H acid group.[52]

The spectra of the other copolymers of SSMA and SSC also indicate that insertion of sulfonic groups occurred after sulfonation. All of the spectra contain characteristic bands of the substitution of aromatic hydrogens by a sulfonic group from the acetyl sulfate.

Elemental Analysis of the Sulfonated Copolymers

The sulfonation degree results obtained by elemental analysis, calculated from the mass percentage of sulfur contained in the copolymers, are presented in Table III. In general, it can be seen that the sulfonation method used was effective regarding insertion of sulfonic groups in the aromatic ring present in the chain of both copolymers. In some cases (SSMA-mass3, SSMA-mass4, SSMA-sol1, SSMA-sol2, and SSC-mass2), with sulfonation times longer than 60 min, the sulfonation degree did not behave as expected; that is, there was greater substitution of aromatic hydrogens by the sulfonic acid groups with longer contact time between the sulfonation species and copolymer. According to the literature, this behavior can be related to the desulfonation process with increasing contact time because sulfonation is a reversible process.[39]

Solubility Tests of the Synthesized Copolymers

The solubility tests were performed to the SSMA and SSC copolymers, with and without the insertion of sulfonic groups in their structures. Table IV presents the solubility results for each copolymer. In general, the solubility results are consistent with the sulfonation degree values reported in Table III.

The solubility results for the copolymer SSMA-mass1, without sulfonic groups, show that it had solubility in a narrower range of δ values (16.86 to 21.4 MPa$^{1/2}$) than the other copolymers without sulfonation. This behavior is consistent with its less amphiphilic character, which is due to the balance between the aromatic groups and the long-chain ester groups in the composition (95/5). In other words, this copolymer had the lowest concentration of long apolar hydrocarbon chains.

Copolymer SSMA-mass2, without the presence of a sulfonic group, presented amphiphilic characteristics, which can be related to its solubility in solvents having a wide range of solubility parameters (15.56 to 22.0 MPa$^{1/2}$). The correlation of the solubility results with the sulfonation degree (Table III) of the sulfonated SSMA-mass2 copolymer indicates a consistent behavior because

Table III. Sulfur Content for SSMA and SSC Copolymers Submitted to Sulfonation Reaction

Sulfonation time (min)	Degree of sulfonation (%)								
	SSMA-mass1	SSMA-mass2	SSMA-mass3	SSMA-mass4	SSMA-mass5	SSMA-sol1	SSMA-sol2	SSC-mass1	SSC-mass2
15	24.68	16.65	20.50	23.78	23.78	21.60	19.30	14.76	22.01
30	39.07	19.60	50.39	26.04	20.64	24.44	20.04	27.97	22.35
60	55.04	32.79	55.88	70.67	27.56	41.62	31.71	31.08	40.24
90	55.71	38.91	46.62	66.64	34.40	71.91	40.34	21.34	62.00
120	68.91	57.40	61.81	51.38	28.48	58.24	30.63	27.12	50.58

Table IV. Solubility of Copolymers in Solvent Systems of Different Solubility Parameters

Polymer sample	Sulfonation degree (%)	Solubility (MPa$^{1/2}$)																			
		15.3	15.56	15.82	16.34	16.86	18.24	18.42	18.66	18.68	19.08	19.46	19.5	19.46	20.8	21.4	22.0	22.6	22.9	23.2	23.5
SSMA-mass1	0																				
	24.68																				
	39.07																				
	55.04																				
	55.71																				
	68.91																				
SSMA-mass2	0																				
	16.65																				
	19.60																				
	32.79																				
	38.91																				
	57.40																				
SSMA-mass3	0																				
	20.50																				
	46.62																				
	50.39																				
	55.88																				
	61.81																				
SSMA-mass4	0																				
	23.78																				
	26.04																				
	51.38																				
	66.64																				
	70.67																				
SSMA-mass5	0																				
	20.64																				
	23.78																				
	27.56																				
	28.48																				
	34.40																				
SSMA-sol1	0																				
	21.60																				
	24.44																				
	41.62																				

Table IV. *Continued*

Polymer sample	Sulfonation degree (%)	Solubility (MPa$^{1/2}$)																		
		15.3	15.56	15.82	16.34	16.86	18.24	18.42	18.66	18.68	19.08	19.5	19.46	20.8	21.4	22.0	22.6	22.9	23.2	23.5
	58.24																			
	71.91																			
SSMA-sol2	0																			
	19.30																			
	20.04																			
	30.63																			
	31.71																			
	40.34																			
SSC-mass1	0																			
	14.76																			
	21.34																			
	27.12																			
	27.97																			
	31.08																			
SSC-mass2	0																			
	22.01																			
	22.35																			
	40.24																			
	50.58																			
	62.00																			

■ Soluble
□ Nonsoluble

the increase in the concentration of sulfonic groups makes the copolymer insoluble in solvent with lower δ values and at the same time increases its solubility at δ values higher than the range mentioned above. Just as for the SSMA-mass2 copolymer, SSMA-mass3 and SSMA-mass4 also showed broad solubility ranges (15.3 to 22.0 MPa$^{1/2}$ and 15.3 to 22.0 MPa$^{1/2}$, respectively). With respect to SSMA-mass3 with sulfonation degree greater than 50.39%, the same solubility behavior is observed in solvents with higher δ values (22.9 MPa$^{1/2}$). This result is in line with the sulfonation degree values obtained, which are mutually similar. At lower δ values, an exception is observed in SSMA-mass3 with a sulfonation degree of 50.39%, which presented solubility starting at 15.82 MPa$^{1/2}$; the others were only soluble in solvents with a solubility parameter greater than or equal to 16.86 MPa$^{1/2}$. This behavior can be explained by the collaboration of part of the copolymer molecules without sulfonation in dissolving the sulfonated molecules because the sulfonation process is random, enabling the distribution of sulfonic acid groups in the copolymer's structure to be highly heterogeneous.[51]

The solubility test results also were consistent with the sulfonation degree results for copolymer SSMA-sol1. Note that this sample, with the highest sulfonation degree (71.91%), was soluble in the range between 18.24 and 22.9 MPa$^{1/2}$, which is higher than that of the other samples.

Analysis of the solubility results for copolymers SSMA-mass5 and SSMA-sol2 showed solubility in a broader range for SSMA-mass5, which is characteristic of amphiphilic molecules. In relation to the sulfonation degree, there is consistency, mainly in the upper solubility limits, because sample SSMA-mass5 with a maximum sulfonation degree (34.40%) presented higher solubility at higher δ values (22.0 MPa$^{1/2}$). In turn, the samples of SSMA-sol2 with and without sulfonic groups showed solubility in a narrower range than did SSMA-mass5. This can be related to the higher molar mass of SSMA-sol2 (123,000 g/mol) or a difference in the distribution of the sulfonic groups in the chain.

Finally, analysis of the solubility results of the copolymers of styrene and stearyl cinnamate SSC-mass1 and SSC-mass2 (styrene/cinnamate compositions of 93/7 and 85/15, respectively), with and without sulfonation, showed that the solubility behavior of the nonsulfonated samples is in line with their compositions: the copolymer with the highest concentration of long hydrocarbon chains (SSC-mass2) was soluble in a broader range (15.82 to 22.6 MPa$^{1/2}$) than that with a low concentration of apolar groups (SSC-mass1), which had a solubility range of 15.82 to 22.0 MPa$^{1/2}$. In relation to the sulfonated copolymers, the solubility of SSC-mass2 was influenced only when the copolymer has a sulfonation degree higher than 50%, in which case the solubility range was shifted (as expected) to higher ranges than for 15% sulfonation. This suggests that copolymers of this type with a lower concentration of long hydrocarbon chains become more susceptible to solubility variation with insertion of relatively low concentrations of polar groups. The more polar character assumed by the sulfonated SSC-mass1 sample is shown by its solubility in solvents with higher parameters: the sample with 31.08% sulfonation was soluble in solvents with δ values up to 23.2 MPa$^{1/2}$.

CONCLUSIONS

We obtained copolymers made of SSMA and SSC with varied compositions and sulfonation degrees, generating a family of copolymers with distinct hydrophilic–lipophilic balances. Of the SSMA copolymers, those with a higher concentration of styrene without sulfonic groups were less amphiphilic and were soluble in narrow ranges of δ values. In contrast, the copolymers with a lower concentration of styrene without sulfonic groups were more amphiphilic and were soluble in broader ranges. The increase in the sulfonic groups in the molecule made the copolymer insoluble in solvents with lower δ values and increased the solubility at higher δ values. Comparing the SSMA copolymers with the same proportions between monomers showed that the one with the highest molar mass presented solubility in a narrower range. On the other hand, of the SSC copolymers without sulfonation, that with the highest hydrocarbon chain concentration had a wider range of δ values, while with sulfonation, the more polar copolymer was soluble in solvents with higher δ. In general, with increasing polar group content, the solubility is not only displaced for solvents with higher solubility parameter, but the range in which the polymer is soluble becomes narrower.

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