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SURFACTANTES REACTIVOS Y EL EFECTO SOBRE LA SINDIOTACTICIDAD DE POLIESTIRENO SINTETIZADO MEDIANTE POLIMERIZACIÓN EN MICROEMULSIÓN

REACTIVE SURFACTANTS AND THE EFFECTS ON SYNDIOTACTICITY OF POLYSTYRENE SYNTHESIZED BY MICROEMULSION POLYMERIZATION

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Resumen

Se polimerizó estireno utilizando Hitenol BC10 (HBC10), Hitenol BC30 (HBC30), Noigen RN20 (NRN20), Noigen RN30 (NRN30) y Noigen RN50 (NRN50) como surfactantes reactivos y persulfato de amonio como iniciador. Los diámetros de partícula (Dp) y las distribuciones de tamaño de partícula (PSD) se determinaron mediante dispersión de luz dinámica, mientras que la tacticidad de los polímeros se analizó en términos de secuencias de tríada a través de resonancia magnética nuclear ^{13}C (^{13}C-NMR). Las masas molares (Mw) y la temperatura de transición vítrea (Tg) de los polímeros se determinaron mediante cromatografía de permeación en gel (GPC) y calorimetría diferencial de barrido (DSC), respectivamente. Se observaron conversiones cercanas al 95% cuando se utilizaron los surfactantes HBC10 y HBC30, mientras que alcanzaron prácticamente el 100% de lconversión de monómero para NRN30 y NRN50. Para el NRN20 se percibió una inhibición a los 15 minutos de reacción alcanzando solo el 80 % de conversión, lo que se atribuyó a eventos de transferencia de cadena. Los Dp estuvieron en el rango de 31 nm a 46 nm, aumentando con la longitud de la cadena de polioxietileno en la serie de surfactantes reactivos. Se obtuvieron Mw entre $7.5x10^5$ y $2.9x10^6$ g/mol. Los porcentajes de sindiotacticidad estuvieron en el intervalo de 55 % a 64 %, los cuales son superiores al 50 % observado al utilizar el surfactante convencinal dodecilsulfato de sodio. La formación de Diadas siguió el comportamiento de probabilidad Bernoulliano.

Palabras clave: surfactantes reactivos, tacticidad, microemulsión, poliestireno sindiotáctico

Abstract

Styrene was polymerized using Hitenol BC10 (HBC10), Hitenol BC30 (HBC30), Noigen RN20 (NRN20), Noigen RN30 (NRN30), and Noigen RN50 (NRN50) as reactive surfactants, and ammonium persulfate as initiator. Particle diameters (Dp) and particle size distributions (PSD) were determined by dynamic light scattering, whereas polymers tacticity were analyzed in terms of triad sequences through ^{13}C nuclear magnetic resonance (^{13}C-NMR). Molar masses (Mw) and glass transition temperature (Tg) of polymers were determined by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC), respectively. Conversions near to 95% were

observed when using HBC10 and HBC30 surfactants, while practically 100% of monomer conversions were achieved for NRN30 and NRN50. For the NRN20 an inhibition was perceived after 15 minutes of reaction reaching only 80 % conversion, which was ascribed to chain transfer events. Dp were in the range of 31 nm to 46 nm, increasing with the length of polyoxyethylene chain in the reactive surfactant's series. Mw between 7.5×10^5 and 2.9×10^6 g/mol were obtained. Syndiotacticity percentages were in the interval of 55 % to 64 %, which are higher than the 50 % observed when using sodium dodecyl sulfate surfactant. Diads formation followed Bernoullian probability behavior.

Keywords: Polymerizable surfactant, tacticity, microemulsion, syndiotactic polystyrene.

Introduction

Tacticity of polymers has marked effect on its physical properties such as melting point (T_m), glass transition temperature (T_g), and mechanical strength. Isotactic polystyrene (i-PSty) is a semicrystalline polymer with a melting point of 240 °C whereas syndiotactic polystyrene (s-PSty) is highly crystalline and has a melting point of 270 °C and a high elasticity modulus [1, 2]. On the other hand, atactic polystyrene (a-PSty) has an average T_m of 240 °C; it is fully amorphous with T_g of 85 °C, brittle, and with poor impact strength [3].

Syndiotactic polystyrene is an engineering plastic synthesized for the first time in 1985 by Ishihara et al. [4, 5]. It has fast crystallization rate, around two orders of magnitude greater than isotactic polystyrene, which is important during polymer processing, for example, s-Psty has a narrow molecular weight distribution, so that, upon cooling from melt, forms a crystalline structure that appears as tightly packed spherulites. Density of both the amorphous and the crystalline regions is approximately 1.05, favoring isotropic part shrinkage and enhance dimensional stability. Their exceptional balance between mechanical and dielectric characteristics, solvent and heat resistance give s-Psty a wide application range [6, 7]. However, several drawbacks exist for its practical use, for example s-PSty needs to be processed at temperatures higher than 290 °C due to its melting point of 270 °C, which is near to its degradation temperature. Also, the fragility of syndiotactic polystyrene can be disadvantageous when mechanical properties are of importance [8]. s-PSty displays complex polymorphic behavior depending on the applied stimuli as temperature or solvent. Also, mechanical properties of s-PSty are related to the degree of crystallinity as well as the crystalline modification that develops during processing of the material [9-13].

Stereoregular polymers can be produced by anionic or transition metal mediated polymerizations. Ishihara et al. [4] synthesized s-PSty using an organometallic catalytic system based on titanium and methylaluminoxane obtaining a polymer 98 wt.% 2-butanone insoluble (percentage of Psty insoluble in 2-butanone is considered a measure of the syndiotacticity percentage), weight-average molecular weight of 82,000 g/mol, and T_m of 270 °C, which enabled advantageous processing of the stereoregular polymer by extrusion and injection molding. Transition metal mediated polymerization methods require special reaction conditions, expensive reagents, and have limited scope. Alternatively, radical polymerization provides a robust and a cheaper route to produce high yielding polymers but has the disadvantage that it provides poor control on polymers tacticity [2].

Some researchers as Matyjaszewski and Davis [14], or Satoh and Kamigaito [15] agree that the key of using radical polymerization for the synthesis of s-PSty would be a controlling compound which could give the exceptional tacticity control given by transition metal complexes but through radical polymerization [2]. For example, Smith and Coote [2] studied the effect of solvent and temperature on polymer tacticity in radical polymerization of methyl methacrylate and styrene, they found that tacticities of polystyrene obtained in this way are almost independent of temperature, and that both polymers are slightly syndiotactic; this tendency was much weaker in polystyrene than in poly(methyl methacrylate). Also, they observed that the studied solvents had little effect on tacticities of each polymer, implying that monomer-polymer interactions in bulk polymerizations do not have important effect on polymers tacticity.

On the other hand, conventional surfactants are widely used in many applications due to their ability to influence the properties of surfaces and interfaces [16]. In the synthesis of polymeric latexes by dispersion, emulsion, miniemulsion or microemulsion polymerization systems, surfactants strongly affect particle nucleation, monomer droplets emulsification, polymer particles stabilization throughout polymerization and the stability of products [17-20]. Some negative effects of the presence of conventional surfactants in latex are foaming and migration during film formation, giving water-sensitivity [21]. These deficiencies can be reduced or eliminated by covalent bonding of reactive surfactant molecules into the latex particles [22].

Reactive surfactants are amphiphilic molecules with an additional functionality that provides it with chemical reactivity and have been widely used since the early 1990s in heterophase polymerization [23, 24]. They can be used as surfmers, inisurfs, or transurfs, and are covalently bonded to the polymer chain, avoiding migration of surfactants in the final application and preventing the formation of hydrophilic spots of high-water absorption, which is undesirable for hydrophobic coatings applications [25]. The use of reactive surfactants in the polymerization of different monomers has been reported elsewhere [26-29], and colloidal properties of latexes, polymerization kinetics, and molar mass of polymers have been analyzed. However, there are no reports in the open literature, about the effects of reactive surfactants on polymers tactiticty. Therefore, in this work, we have synthesized polystyrene through radical polymerization in microemulsion in the presence of the reactive surfactants Hitenol BC10, Hitenol BC30, Noigen RN 20, Noigen RN 30, and Noigen RN 50 (Figure 1), and studied their effect on syndiotacticity of resulting polystyrene.

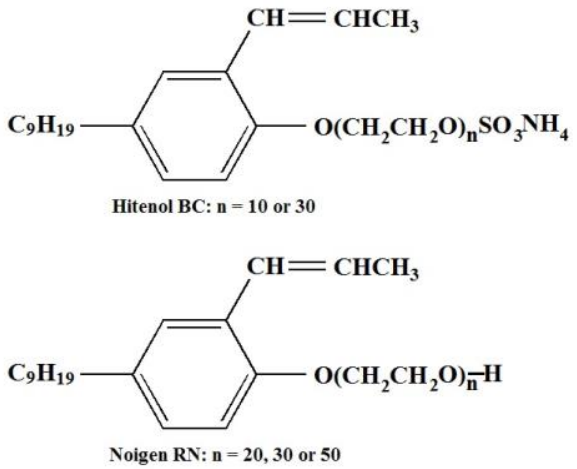

Figure 1 Chemical structure of reactive surfactants used in styrene polymerization.

Experimental

Materials

Sodium dodecyl sulfate (SDS) was purchased from Hycel (Guadalajara, Mexico) (≥ 98 %) and used as conventional surfactant. Reactive surfactants Hitenol BC10, Hitenol BC30, Noigen RN 20, Noigen RN 30, and Noigen RN 50 were generously provided by Dai-Ichi Kogyo Seiyaku Co., Ltd. (Japan) (> 98 %), through Montello, Inc. (Tulsa, USA). Ammonium persulfate (APS) and styrene monomer (Sty) were purchased from Sigma-Aldrich (Toluca, Mexico) (≥ 99 %). APS was used as received, while Sty was distilled under reduced pressure to remove inhibitors and stored in the dark at 2 °C before used. Distilled grade water and argon of ultrahigh purity from Infra™ were used in all the experiments.

Polymerizations

Polymerizations were carried out at 60 °C and 200 rpm in a two-neck 250 mL glass-jacketed reactor with sampling valve, equipped with magnetic stirring and a reflux condenser. The water (150 g), APS (120 mg) and surfactant (3.0 g) SDS, Hitenol BC10, Hitenol BC30, Noigen RN 20, Noigen RN 30, or Noigen RN 50 (3.0 g) were charged to the reactor; next, the system was cooled to 15 °C and purged with argon for 1 h to remove oxygen. Then, the mixture was brought to the reaction temperature by passing hot water through the reactor jacket during 10 min; at this point, the styrene monomer (6.12 g) was added to the reactor using a gas tight syringe in one shot to start polymerization. Reactions were allowed to proceed for 1 h. Conversions were gravimetrically determined withdrawing samples from the reacting system at given times and placed in vials (of known weight) and immersed into an ice bath to stop polymerization. Then, samples were weighed and dried at 60 °C in an oven by 48 h. Conversions were calculated from a mass balance. Polymer samples were labelled as PSty-HBC10, PSty-HBC30, PSty-NRN20, PSty-NRN30, PSty-NRN50, and PSty-SDS, corresponding to PSty obtained in the presence of each surfactant.

Characterization

Particle size was determined by quasi-elastic light scattering (Nano S90 apparatus, Malvern, UK) at 25 °C. Polymer samples taken for gravimetry were purified washing several times with hot water to remove surfactants and initiator and dried at 40 °C for molar masses determinations. Average molar masses and molar masses distributions of polymers (previously dissolved in THF at 1 mg/mL) were determined in a gel permeation chromatograph apparatus (USA, Alliance Waters, 2695) with two PLgel Mixed C 5µ columns and at a flow rate of 1 mL/min, with a refraction index detector.

Tacticities of polystyrene samples were determined in terms of triads by ^{13}C-NMR (JEOL ECA600

Spectrometer, 600 MHz). Approximately 50 mg of each sample were dissolved in 0.7 mL of deuterated chloroform ($CDCl_3$) and analyzed at the carbon frequency of 150.86 MHz. Tacticity was determined by the areas of spectra signals corresponding to *para*-aromatic carbon of the PSty samples between 125 to 126.5 ppm according to Ziaee *et al*. [30] by means of deconvolution function included in the NMR Delta 5.0.3 program from JEOL. In those signals it was possible to evaluate the presence of every stereochemical configuration (syndiotactic (rr), atactic (mr) and isotactic (mm)) in the samples. Syndiotacticity percentage (rr) of each polymer sample was calculated using equation (1):

$$RR = \frac{A_{rr}+\frac{1}{2}A_{rm}}{A_T} \times 100 \quad (1)$$

where $A_{(rr)}$ and $A_{(rm)}$ represents the values of the areas of signals corresponding to syndiotactic and atactic configurations, respectively. A_T is the sum of all areas that comprise the tacticity of polymer in each region of spectra ($A_{(rr)}$ + $A_{(rm)}$+ $A_{(mm)}$) [31, 32].

Differential scanning calorimetry (DSC) analyses were carried out in a calorimeter (Q200, TA Instruments, USA). Dried samples of 5–10 mg were encapsulated in standard aluminium pans. Thermograms were recorded at a heating rate of 5 °C/min over a range of 25–250 °C.

Results and discussions

Kinetics of polymerization

The effects on polymerization kinetics of Hitenol BC series surfactants which are polyoxyethylene alkylphenyl ethers ammonium sulfate (anionic type), and Noigen RN surfactants which are polyoxyethylene alkylphenyl ethers (nonionic type) (shown in Figure 1) were studied. Figure 2 shows conversion as a function of time obtained in styrene polymerization using the different reactive surfactants. It can be observed that conversions were near 95 % for HBC10 and HBC30, whereas for Noigen RN30 and RN50 almost 100 % conversion was achieved. It is noticeable that, for Noigen RN20, after 15 min of polymerization conversion reaches only 80 % (Figure 2b).

It can be seen from Figure 2a that conversion and polymerization rate are higher for HBC10 than for HBC30 at low reaction times; however, after 10 min of polymerization, conversions are slightly higher for HBC30. It has been previously reported [29, 34] that chain transfer reactions to the allyl double bond of reactive surfactants occurs decreasing polymerization rate; thus, chain transfer events are more marked for HBC10 at high conversions. The anionic nature of HBC surfactant series has an important effect on kinetics of Sty polymerization, comparing HBC30 with Noigen RN30, higher conversions were obtained for Noigen surfactant; the main difference between both molecules is that NRN are anionic.

Particle sizes and molar masses

Table 1 shows that the average particles diameters (Dp) when using HBC10 and 30 reactive surfactants, were 38 and 43 nm, whereas for the non-ionic surfactants, Dp's were 46, 44 and 46 nm, for the Noigen RN20, 30 and 50, respectively. By comparing Dp for particles prepared with surfactants HBC30 and Noigen RN30 (same number of ethylene oxide units) it is observed that Dp are similar, thus ionic nature of these two surfactants does not affect final Dp. When using SDS as conventional surfactant Dp was 31 nm; SDS is an smaller molecule than the reactive surfactants here studied, this means that closer packing occurs with SDS, resulting in smaller particles.

Figure 3 shows the corresponding particle-size distributions (PSD). PSD of latexes were monomodal except for the one obtained with Noigen RN20 which showed bimodal PSD. This behavior can be attributed to particle instability and coagulation. Latexes synthesized in presence of HBC10 and HBC30 were like that obtained with SDS. Rios et al. [27] studied the effect of HBC10 and NRN10 concentration on Dp in the Sty/butyl acrylate emulsion polymerization, observing Dp between 144 nm and 152 nm, depending on the surfactant concentration.

On the other hand, Mekki et al. [35] studied the effect of 4-phenylbutyl maleate and 7-phenylheptyl maleate as reactive surfactants on styrene emulsion polymerization. They found that final polymerization conversions increase with the chain length of the hydrophobic alkyl part, whereas Dp decreases with the hydrophobic chain length and surfactant concentration, ranging from 73 to approximately 700 nm, depending on the surfactant type and its concentration. This behavior is contrary to that observed in the present work.

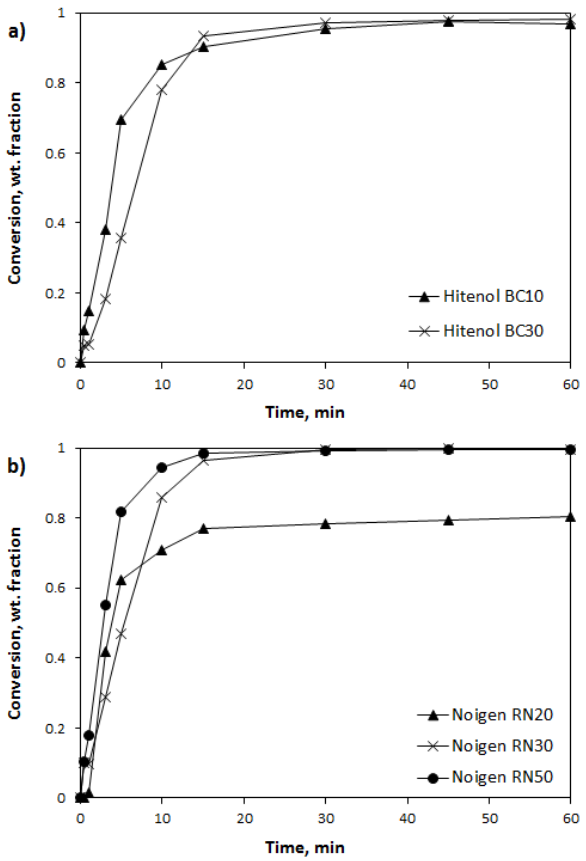

Figure 2 Conversion fractions *vs*. time for styrene polymerization in the presence of the different reactive surfactants.

The weight average molar masses (Mw) of final PSty's were in the range of 0.75×10^6 g/mol to 2.9×10^6 g/mol (Table 1). Figure 4 shows the corresponding MMD, where MMD are relatively wide in all cases with dispersity indexes in the range of 2.3 < Mw/Mn < 4.4 (Table 1) and independent of PEO length for HBC series, while for Noigen series, dispersity index decreased with the PEO length. In all cases bimodal MMD were observed, however for PSty obtained with NRN20 the molar mass population corresponding to high molar masses values was more evident. This also supports the assumption of particles coagulation as observed in Figure 3 for this surfactant, resulting in the higher Mw values due to bimolecular radical annihilation. In a previous work [29], where methyl methacrylate was polymerized in the presence of HBC10, we found Dp in the range of 25 to 40 nm with broader PSD and Mw values between 1.4×10^6 to 2.1×10^6 g/mol with dispersity indexes in the range of 1.5 to 2.1, indicating that solubility of monomer in water and reactivity have a great effect on final polymer characteristics.

Table 1 Average particle diameter of final latexes, weight average molecular weight and polydispersity index (*Mw*/*Mn*) of final polymers.

Sample	***Dp*, nm**	***Mw*×10^{-6} g/mol**	***Mw*/*Mn***
PSty-HBC10	38	1.46	2.9
PSty-HBC30	43	2.30	2.9
PSty-NRN20	46*	2.90	4.4
PSty-NRN30	44	2.20	2.7
PSty-NRN50	46	2.10	2.3
PSty-SDS	31	0.75	3.3

* This value corresponds to the first peak of PSD shown in Figure 3; Dp of 280 nm was observed for the second peak of PSD in the same Figure for this surfactant.

Polymers stereochemistry and Tg

The effects of hydrophobic alkyl part for a same reactive surfactant series, and the ionic character between both reactive surfactant series on PSty tacticities were studied by ^{13}C-NMR analysis. It has been reported that ^{1}H-NMR spectra have better signal to noise and shorter acquisition times, however ^{13}C-NMR remains as the preferred analytical tool due to the significantly larger signal splitting over a wider chemical shift range, which enables distribution data to be more easily extracted from the spectra [2]. A typical ^{13}C-NMR spectrum of polystyrene has five main regions: quaternary aromatic carbon, *ortho* and *meta*-aromatic carbons, *para*-aromatic carbon, methylene region, and methine carbon. In this work, the *para*-aromatic carbon region was used to assess tacticity of PSty [30] (Figure 5), because this region has the advantage that produces spectra of lower complexity where triad splitting is better observed. Besides, signal areas can be better resolved because of the high magnetic field (14 T) of the NMR equipment [36].

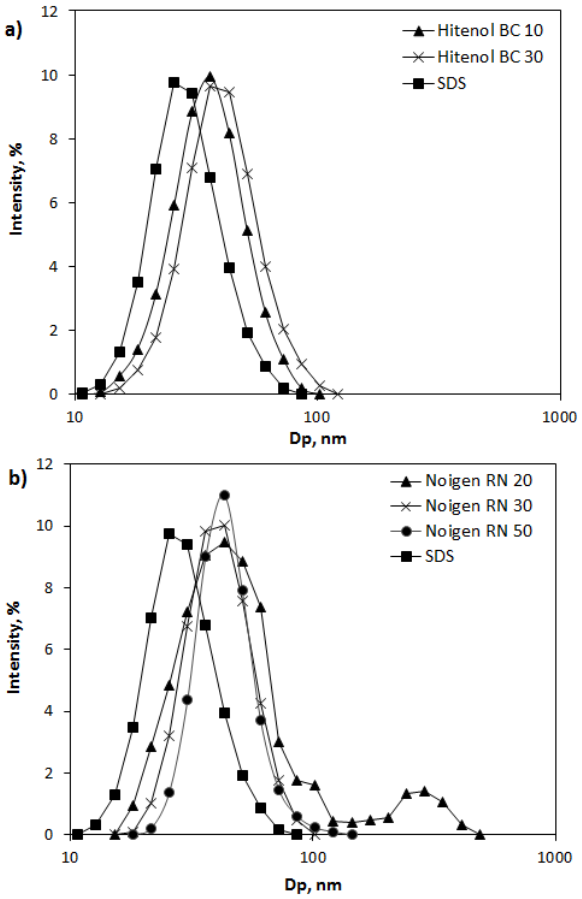

Figure 3 Particle size distributions of final latexes obtained for the different reactive surfactants used.

Table 2 shows the triad fraction (relative areas) of syndiotactic, atactic and isotactic PSty configurations obtained by deconvolution of the areas of the signals of the *para*-aromatic carbon of the spectra shown in Figure 5. Isotactic triad fraction values were similar for HBC30 and Noigen series (mm ≈ 0.20), whereas for HBC10 this value was the lowest (mm = 0.09). In contrast, the highest mm observed value was for PSty obtained using SDS as conventional surfactant. It is noticeable that syndiotactic (rr) values decrease with the length of the hydrophobic alkyl part (PEO) for both surfactant type. This could be explained as the alternated position of the phenyl pendant group in the polymer (syndiotactic configuration) is either disturbed or restricted due to PEO chain length of the surfactant when it is coupled to the polymer backbone during polymerization. It means that longer PEO chains in the reactive surfactant, promotes higher steric effects over any of the spatial planes of the polymer.

Bernoullian probability (P_m) can be used to determine the diad formation through *meso*- or *racemo*- additions of monomer to propagating chain (isotactic or syndiotactic, respectively). Bernoullian model assumes that probability of forming a specific diad is independent of the nature of the previous diads and only one parameter is necessary to specify the stereochemistry. This parameter is P_m, the probability of forming a *meso* addition (therefore P_r, the probability of forming a *racemo* addition is given by 1- P_m), in other words, the lower the P_m value, the higher the syndiotacticity tendency. For a Bernoullian behavior, the sum of probability of forming a *racemo* diad given a prior *meso* diad (P_{mr}) and the probability of forming a *meso* diad given a prior *racemo* diad (P_{rm}) is equal to 1. In this work, Bernoullian probabilities were calculated with equations (2) to (4) [2]:

$$P_m = mm + 0.5rm \quad (2)$$

$$P_{mr} = \frac{rm}{2mm+rm} \quad (3)$$

$$P_{rm} = \frac{rm}{2rr+rm} \quad (4)$$

where *mm*, *rm* and *rr* are the triad fractions shown in Table 2.

Table 3 shows the calculated Bernoullian probabilities, percentage of tacticity determined from the areas of the *para* carbon signals of PSty samples using the equation 1, and the Tg values determined from DSC analysis shown in Figure 6. It can be seen from Table 3 that polymerizations follow a Bernoullian behavior (P_{mr} + P_{rm} ≈ 1.0) for the reactive surfactants, except when using NRN20 and the conventional SDS surfactant. PSty with the lower *meso* addition tendency was that synthesized in the presence of HBC10 surfactant giving a syndiotacticity of 64 %. By using the typical SDS surfactant a 50 % of syndiotacticity was observed. Comparing the HBC series reactive surfactant, syndiotacticity decreases with the PEO length of surfactant, while Tg increases. Similar behavior was observed changing from NRN20 to NRN30 (62 % to 55 % of syndiotacticity, respectively), but increasing the PEO length of reactive surfactant to 50 units (NRN50), syndiotacticity increased to 58 %. On the other hand, comparing HBC30 with NRN30 syndiotacticity resulted in 55 %, therefore we can conclude that under the studied conditions ionic charge of surfactant does not affect PSty stereochemistry.

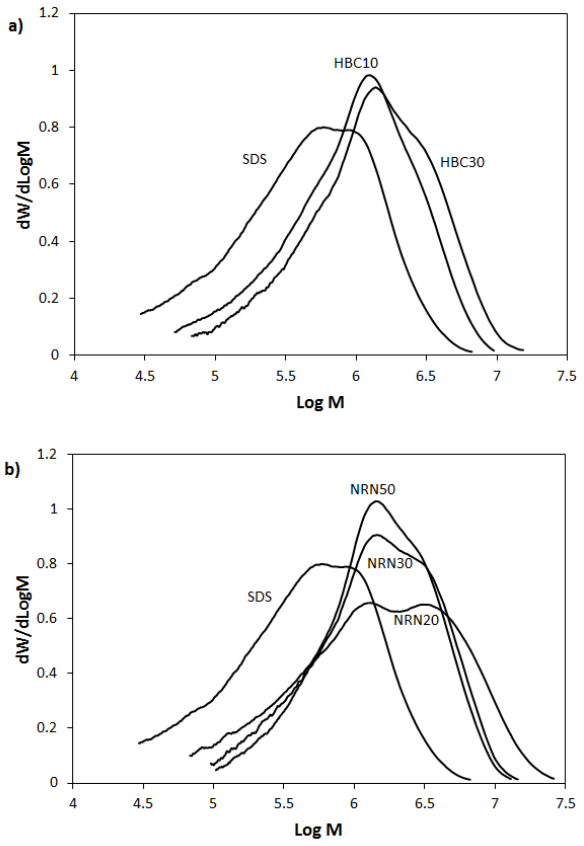

Figure 4 Molar masses distributions (MMD) of the polymers at the end of reaction for the different reactive surfactants used.

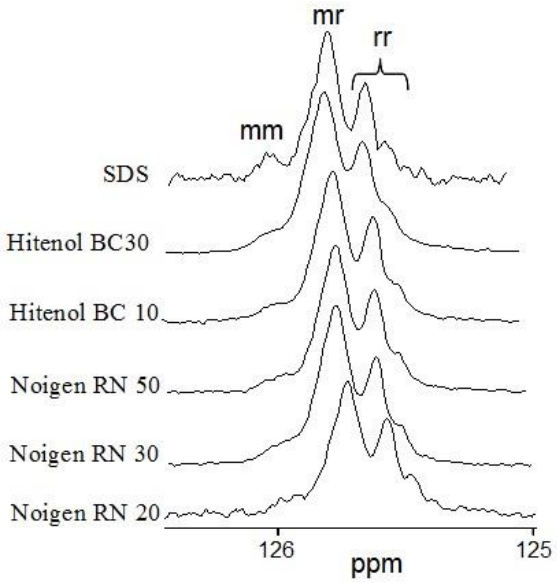

Figure 5 ^{13}C-NMR spectra in the zone of the carbonyl group showing the signals corresponding to rr, rm, and mm triads (syndiotactic, atactic, and isotactic, respectively) of final polymers synthesized with the different reactive surfactants.

Table 2 Observed triad fractions (relative areas) of PSty samples calculated from the areas of the signals of the *para*-aromatic carbon of the ^{13}C NMR spectra (Figure 5).

Triad sequence	**Triad tacticity fraction**					
	PSty-HBC10	PSty-HBC30	PSty-NRN20	PSty-NRN30	PSty-NRN50	PSty-SDS
rr	0.36	0.30	0.43	0.30	0.32	0.27
rm	0.55	0.50	0.39	0.52	0.50	0.45
mm	0.09	0.20	0.19	0.19	0.17	0.28

rr = syndiotactic, rm = atactic and mm = isotactic

Table 3 Bernoullian probabilities, tacticity % determined from the areas of the *para* carbon signals of PSty samples according to equation 1, and Tg values determines by DSC analysis.

Sample	P_m	P_{mr}	P_{rm}	$P_{mr} + P_{rm}$	P_r of *para* aromatic	Tg, °C
PSty-HBC10	0.36	0.753	0.433	1.19	64	88.5
PSty-HBC30	0.45	0.556	0.455	1.01	55	91.8
PSty-NRN20	0.38	0.506	0.312	0.82	62	79.3
PSty-NRN30	0.45	0.578	0.464	1.04	55	97
PSty-NRN50	0.42	0.595	0.439	1.03	58	84.5
PSty-SDS	0.50	0.446	0.455	0.90	50	95

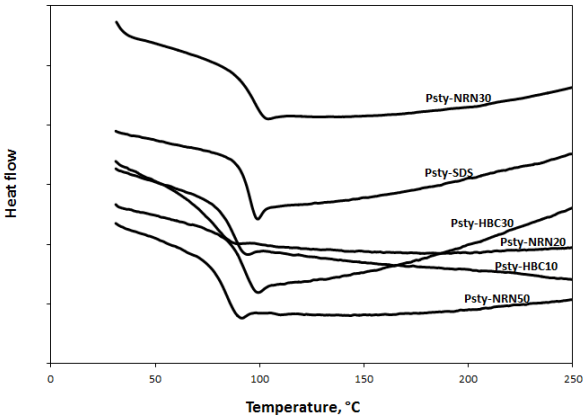

Figure 6 Heat flow versus temperature obtained from DSC analysis of final polymers for the different reactive surfactants used.

Conclusions

Styrene was polymerized using Hitenol and Noigen polymerizable surfactants series. Latexes with Dp in the range of 31 nm to 46 nm, increasing with the length polyoxyethylene (PEO) chain in the HBC and NRN surfactants with monomodal PSD, except for NRN20 surfactant (which was bimodal) were obtained. PSty with Mw between 7.5×10^5 and 2.9×10^6 g/mol were obtained. Syndiotacticity percentages were in the interval of 55 % to 64 %, which are higher than the 50 % observed when using the conventional sodium dodecyl sulfate (SDS) surfactant. The higher syndiotacticity percentage of PSty was that obtained using HBC10 as reactive surfactant. Organometallic catalyst typically used in the synthesis of s-PSty produce polymer with syndiotacticity as high as 98 %, the use of reactive surfactants could be a cheaper alternative to synthesize s-PSty if polymerization process is optimized, i.e. polymerization mode (semicontinuous or continuous), reaction temperature, initiator concentration or surfactant amount.

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