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Novel Gemini-Type Reactive Dispersants Based on PS/PEO Block Copolymers: Synthesis and Application

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ABSTRACT: In this paper, the possibilities offered by anionic polymerization were exploited to engineer well-defined PS-*b*-PEO$_2$ gemini-type dispersants that were fitted with terminal styrenic groups. Two routes were explored to obtain this novel generation of surfactants whose thorough characterization indicated that they exhibit the expected molecular structure. These reactive block copolymers have been subsequently used as surfactants in the emulsion polymerization of styrene to stabilize the colloidal particles formed. The kinetics of polymerization in the presence of such reactive surfactants were shown to differ from the case involving PS-*b*-PEO linear macromonomers as surfactants.

Introduction

There are strong incentives to substitute polymerizable dispersing agents for unreactive homologues in polymerizations that require the presence of emulsifiers to stabilize the polymer particles formed.[1−4] The advantages are multifold: upon immobilization of this emulsifier on the surface of particles, one can prevent its adventitious desorption under stress or its migration when filming the latexes. If the polymerizable emulsifier is in addition an amphiphilic block copolymer, its macromolecular size can provide the particles with steric stabilization beside the electrostatic stabilization that would result from the choice of a charged block as hydrophilic moiety. Considering their ability to self-assemble in a selective solvent for one of the two blocks, amphiphilic block copolymers appear at first glance as excellent substitutes for classical surfactants that are also known to be wastewater pollutants. In particular, in applications that require the absence of any charge, amphiphilic copolymers constituted of a nonionic block that is able to stabilize particles by steric repulsion attract much interest.

However, the role of an emulsifier in emulsion polymerization is multifold and complex:[5,6] not only is it essential to stabilize the particles formed but also it is strongly involved in the particle nucleation and growth so that one cannot contemplate the substitution of macromolecular dispersants for classical ones without profoundly affecting the entire polymerization process. In particular, the dynamics of exchange of amphiphilic species that self-assemble into a micellar structure is much slower for block copolymers than for classical surfactants, resulting in totally different lifetimes of the corresponding micelles.[7−10]

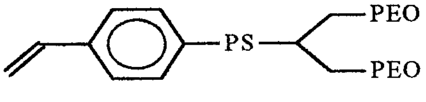
As an extension of a previous study[11] devoted to the functionalization of PS latexes by linear PEO-*b*-PS-based macromonomers, this paper is the second of a series that aims at investigating the influence of the molecular architecture of this family of macromonomers on the outcome of polymerization carried out in dispersed media. The fact that dimeric or gemini-type surfactants exhibit better wetting, foaming and dispersing performances than conventional surfactants[12] prompted us to examine the potential of gemini-type PS-*b*-PEO$_2$ macromonomers as reactive emulsifiers and compare their behavior with that of linear homologues. This contribution is more specifically devoted to their use in the emulsion polymerization of styrene, aspects pertaining to their role in dispersion polymerization being part of a further publication. The idea underlying this study is that the gemini architecture may provide better performances in terms of functionalization and stability of the latex particles.

Only very few papers[13] report the synthesis and the use of ionic surfmers that exhibit a gemini structure in emulsion polymerization, and to our knowledge, the use of a nonionic gemini-type macromonomer has never been reported. The reason for this may lie in their syntheses, which require a multiple-step synthesis.

The paper mainly focuses on the synthesis of PS-*b*-PEO$_2$ gemini-type macromonomers fitted with a styrenyl unsaturation. Two routes (1a,b and 2) that allow one to prepare such species with excellent molecular control were explored. The results that were obtained when using these gemini-type reactive surfactants in the emulsion polymerization of styrene are also reported.

Results and Discussion

The self-assembly behavior of amphiphilic block copolymers in aqueous solutions is known to not only depend on the hydrophobic−hydrophilic balance but to be also affected by the fluctuation in the size of the amphiphilic entities: this is why it was decided to rely on the sequential anionic polymerization of styrene and ethylene oxide for the preparation of these gemini-type PS-*b*-PEO$_2$ macromonomers.



G

Two pathways were explored for the synthesis of these gemini-amphiphilic species (*G*) that can also be viewed as miktoarm star copolymers[14,15] constituted of two

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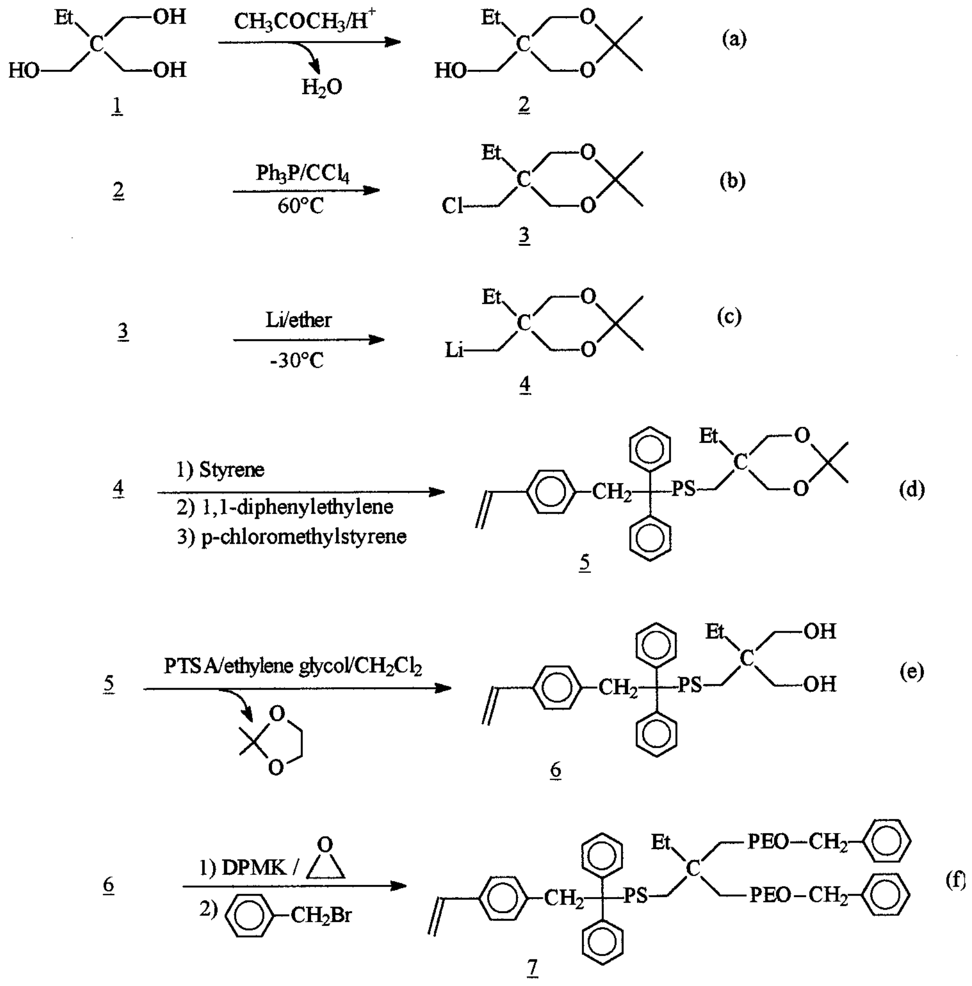
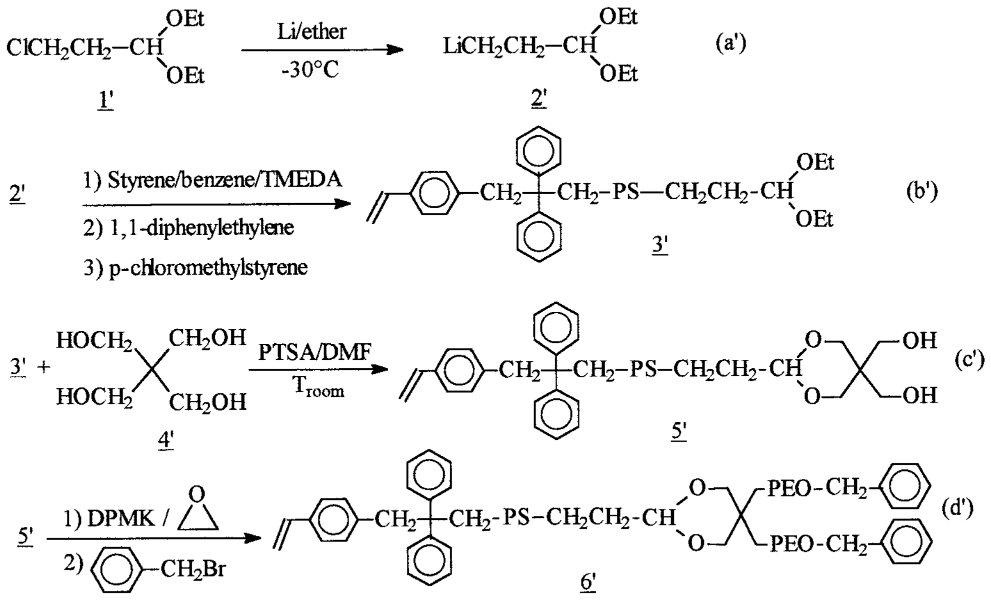
Scheme 1. Synthesis of PS-*b*-PEO$_2$ Gemini-Type Macromonomer via Route 1a



Scheme 2. Synthesis of PS-*b*-PEO$_2$ Gemini-Shaped Reactive Dispersant via Route 1b



identical hydrophilic PEO chains connected to a hydrophobic PS chain. As to their terminal unsaturation, it was introduced at the end of the PS block, the styrenyl group being chosen for this purpose.

The first route (Schemes 1 and 2) consisted in the synthesis of a linear α-acetal, ω-styrenyl polystyrene (**5**, **3′**) and in the subsequent cleavage (eq e) or modification (eq c′) of the α-acetal so as to generate two hydroxyl groups and grow two PEO blocks (eqs f and d′). As to the second route (Scheme 3), it is based on the synthesis of the heterodifunctional polystyrene (**4″**), fitted at one end with an acetal group and a ketal ring at the other; two groups that are respectively expected to release upon selective acidic treatment a primary hydroxyl and

Scheme 3. Synthesis of PS-*b*-PEO$_2$ Gemini-Shaped Reactive Dispersant via Route 2

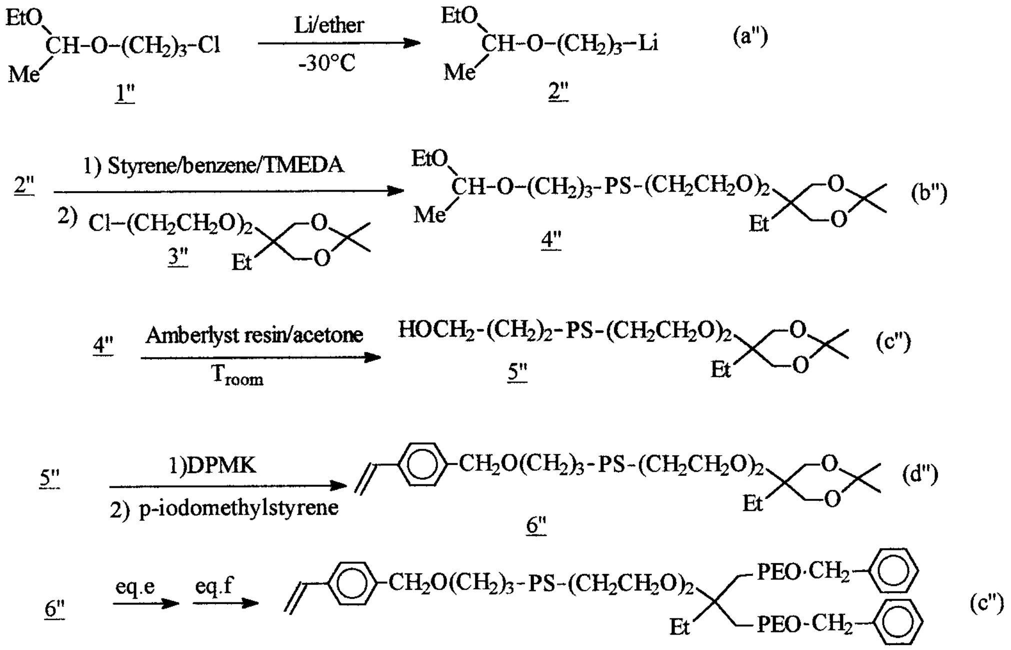


Table 1. Characteristics of *ω*-styrenyl Polystyrene Obtained from Route 1a

$[\text{styrene}]_0/[\text{initiator}]_0$	solvent	*T*, °C	$\bar{M}_{n,PS}$ targeted[a]	$\bar{M}_{n,PS}$ SEC	$\bar{M}_w/\bar{M}_n$ SEC	$\bar{M}_{n,PS}$[b] ^{1}H NMR	efficiency,[c] %
10	benzene	5	1494	3480	1.16	3000	36
10	benzene	25	1494	2680	1.18	2500	47
6	benzene	5	1078	2410	1.17		32
6	benzene	5	1078	2345	1.16		31

[a] Calculated from $[([\text{styrene}]_0/[\text{initiator}]_0)M_{\text{styrene}}] + M_{\text{end}}$, M_{styrene} being the molar mass of the styrene units and M_{end} the molar mass of end groups. [b] Calculated upon taking the ratio of the area of the signal corresponding to the protons of the methylene group of the styrenyl unsaturations (I_1, $\delta(CH_2{=}) = 5.1-5.6$ ppm) to that of the peak arising from aromatic protons (I_2, $\delta = 6.2-7.2$ ppm): $\bar{M}_{n,PS} = 104(2I_2/5I_1)$. [c] Efficiency = $(\bar{M}_{n,PS\ \text{targeted}} - M_{\text{end}})/(\bar{M}_{n,PS\ \text{SEC}} - M_{\text{end}})$.

1,3-diols. These functions were then respectively used to introduce a styrenyl unsaturation and grow two PEO blocks.

Synthesis of Gemini-Type PS-*b*-PEO$_2$ Macromonomers Fitted with a Styrenyl Unsaturation. 1. Route 1a. A first series of gemini-type PS-*b*-PEO$_2$ macromonomers carrying a styrenyl unsaturation at the PS end block were obtained according to Scheme 1.

Starting from the cyclic ketal **2** that was obtained from the reaction of the 1,1,1-tri(hydroxymethyl) propane (**1**) with anhydride acetone in acidic medium (eq a) followed by its chlorination in CCl_4 using triphenylphosphine, the chlorinated compound **3** was lithiated in the presence of a large excess of lithium in ether medium (eq c). Both the high selectivity and efficiency of this last reaction were checked by gas chromatography. The yield of the reaction was very close to 100%.

The anionic polymerization of styrene was then triggered by addition of the initiator solution thus formed into the flask containing the monomer. The medium turned red at once indicative of the formation of styryl carbanions. After complete conversion of monomer, the living carbanionic species were reacted with 1,1-diphenylethylene, the anion of lower reactivity thus formed being deactivated by an excess of *p*-chloromethylstyrene to fit the PS chains with a styrenyl unsaturation (eq d).

All samples have been characterized by size exclusion chromatography (SEC) and ^{1}H NMR spectroscopy (Table 1). The good agreement between molar mass determined by ^{1}H NMR and SEC attested to the good functionalization in styrenyl end group.

Regardless of the experimental conditions used (temperature, solvent), the molar mass of PS samples obtained were about twice as much higher as those targeted, indicating that only 50% of the lithiated initiator has promoted the polymerization of styrene. Nevertheless, all the PS isolated (**5**) exhibited very narrow molar mass distributions.

Once isolated, the *ω*-styrenyl PS macromonomer that also carried a ketal ring in α-position was treated in acidic conditions so as to release its two hydroxyl functions (eq e). The latter reaction was carried out in dichloromethane using *p*-toluenesulfonic acid (PTSA) in the presence of ethylene glycol (whose role was to trap the acetone formed upon cleavage of the ketal of **5** and therefore drive the equilibrium toward the release of the two hydroxyls in **6**), preferably to Amberlyst resin or hydrochloric acid, which was not specific enough: hydrochloric acid reacted both with the ketal ring and the styrenyl unsaturation of **5** whereas the Amberlyst resin failed to cleave the same ketal function under our experimental conditions. The chain end modification using PTSA was checked by SiO_2-based thin-layer chromatography (TLC). Indeed, earlier works[16−19] have reported the possibility of separating functionalized from unfunctionalized polymers by this technique. Polystyrene carrying two hydroxyl end groups could be

Table 2. Characteristics of the PS-*b*-PEO$_2$ Gemini Surfactant Synthesized via Route 1a

$\bar{M}_{n,PS}$ SEC	$\bar{M}_{n,PEO}$[a] targeted	N[b]	$\bar{M}_{n,PEO}$[c] ^{1}H NMR	$\bar{M}_w/\bar{M}_n$ SEC
3480	7000	1.90	7780	1.08

[a] $\bar{M}_{n,PEO} = {}^1/_2(44([\text{ethylene oxide}]_0/\text{m})\bar{M}_{n,PS}$ with m = mass of ω-styrenyl PS. [b] N: number of PEO chains per PS chain, determined from the ratio of methylene protons of the aromatic quenching agent (4.5 6 ppm) to that of methylene protons of the styrenyl unsaturations (5.1−5.6 ppm). [c] Determined from the ratio of oxirane protons (I_1, $\delta(CH_2O) = 3.6$ ppm) to that of aromatic protons of polystyrene (I_2, $\delta = 6.2-7.2$ ppm): $\bar{M}_{n,PEO} = 44(5I_1/8I_2\overline{DP}_{n,PS})$.

separated from those with one or none hydroxyl end group. The elution solvent used was a tetrahydrofuran/hexane (45/55%, v/v). Under these conditions unfunctionalized polystyrene migrated faster than its homologue fitted with one hydroxyl end group, whereas polystyrene end-capped with two hydroxyl end groups did not. The cleavage of the ketal ring in **5** by PTSA was found to be quantitative after 12 h of reaction.

The two hydroxyl groups thus released were subsequently used to grow two poly(ethylene oxide) blocks after being deprotonated by diphenylmethyl potassium, (DPMK) (eq f). Previous studies have proved that alkoxide centers resulting from the deprotonation of 1,3-diols are able to promote the propagation of ethylene oxide.[20] Great care was given to the purification and drying of **6**, any residual protonic impurity being a potential source for the subsequent formation of linear PEO chains. After the complete conversion of ethylene oxide, active centers were deactivated by addition of benzyl bromide. The isolated copolymer was then characterized by ^{1}H NMR; in this way the size of PEO blocks could be determined upon comparing the peak due to the methylene protons of the styrenyl unsaturations (I_3, $\delta(CH_2{=}) = 5.1-5.6$ ppm) with that arising from the methylene protons of the aromatic quenching agent (I_4, $\delta(CH_2Ph) = 4.56$ ppm). Table 2 reports the characteristics of these PS-*b*-PEO$_2$ gemini-type reactive surfactants. The molar masses of the PEO blocks, determined by ^{1}H NMR, were found in good agreement with the expected values. SEC analysis, carried out before and after the growth of PEO blocks, does not show the presence of any homopolymer, either PEO or PS, the traces obtained exhibiting a narrow distribution of molar masses. These results confirm that all reactions carried out occurred as expected.

2. Route 1b. Realizing that the approach followed in the first instance to obtain these gemini-shaped reactive dispersants not only was tedious but also failed to afford PS blocks of precisely targeted size, we explored a simpler way to generate the same species.

Starting from the commercially available 3-chloropropionaldehydediethyl acetal (**1′**), **2′** was readily derived by stirring **1′** in the presence of lithium, the macromonomer **3′** being subsequently obtained upon following the sequence of reactions in Scheme 2.

The sample obtained exhibited narrow molar mass distribution and its experimental molar mass was in good agreement with the targeted one (Table 3). In addition, characterization by NMR indicated that its ω-functionalization by the styrenyl unsaturation occurred quantitatively (Table 3).

To generate 1,3-diols at the end of such PS macromonomer, the latter was reacted with a large excess of pentaerythritol (**4′**) at room temperature in dimethylformamide (DMF) and in acidic medium (eq c′). Under these conditions the terminal acetal function of macromonomer **3′** underwent a transacetalation reaction and gave rise to **5′** with its 1,3-diols. The yield of this reaction was checked by ^{1}H NMR upon comparing the areas of peaks due to methylene protons of styrenyl unsaturation ($\delta(CH_2{=}) = 5.1-5.6$ ppm) with that of the methoxy protons ($\delta CH_2OH = 3.98-3.92$ ppm) (Figure 1). The close to 1 ratio showed that the functionalization of **3′** by pentaerythritol occurred quantitatively generating two hydroxyls at the end of these ω-styrenyl macromonomers. No product resulting from the reaction of two diethyl acetal, ω-styrenyl polystyrene chains with one molecule of pentaerythritol could be detected by SEC. These hydroxyl functions were then deprotonated by DPMK, and the potassium alkoxide formed was used to polymerize ethylene oxide as previously described (eq d′). The agreement between the targeted and the experimental molar masses of these PS-*b*-PEO$_2$ copolymers is excellent as shown in Table 3 and the functionalization close to perfect.

Although straightforward, this synthetic route that afforded samples of precisely controlled functionality and size (in contrast to route 1a) involves however a drawback: these gemini-shaped dispersants contain between their PS and PEO blocks a ketal ring that could be cleaved under strong acidic conditions, precluding their use in such media.

3. Route 2. Route 1b was thus modified in order to circumvent the latter drawback (Scheme 3). Using **2″** as initiator for the anionic polymerization of styrene and following a method previously described,[11] the living carbanionic species formed were deactivated by a purposely designed electrophilic compound containing a ketal ring (**3″**). This end-capping reaction resulted in an excellent yield as evidenced by ^{1}H NMR (Figure 2 and Table 4).

Table 3. Characteristics of the PS-*b*-PEO$_2$ Gemini Surfactant Synthesized via Route 1b

$\bar{M}_{n,PS}$[a] targeted	$\bar{M}_{n,PS}$ SEC	$\bar{M}_w/\bar{M}_n$ SEC	$\bar{M}_{n,PS}$[b] ^{1}H NMR	(acetal end/ styrenyl end)[d]	f[e]	$\bar{M}_{n,PEO}$[g] targeted	$\bar{M}_{n,PEO}$[c] ^{1}H NMR	(benzyl end/ styrenyl end)[f]
2300	2700	1.18	2225	1.04	1.09	12 150	13 580	0.9

[a] Calculated from $[([\text{styrene}]_0/[\text{initiator}]_0)M_{\text{styrene}}] + M_{\text{end}}$, M_{styrene} being the molar mass of the styrene units and M_{end} the molar mass of end groups. [b] Calculated upon taking the ratio of the area of the signal corresponding to the protons of the methylene group of the styrenyl unsaturations (I_1, $\delta(CH_2{=}) = 5.1-5.6$ ppm) to that of the peak arising from aromatic protons (I_2, $\delta = 6.2-7.2$ ppm): $\bar{M}_{n,PS} = 104(2I_2/5I_1)$. [c] Determined from the ratio of oxirane protons (I_1, $\delta(CH_2O) = 3.6$ ppm) to that of aromatic protons of polystyrene (I_2, $\delta = 6.2-7.2$ ppm): $\bar{M}_{n,PEO} = 44(5I_1/8I_2\overline{DP}_{n,PS})$. [d] Determined by ^{1}H NMR from the ratio of acetal protons (I_1, $\delta(CH(OEt)_2) = 4.3$ ppm) to those of methylene group of styrenyl end (I_2, δ $(CH_2{=}) = 5.1-5.6$ ppm): $2I_1/I_2$. [e] $f = I_3/I_4$, I_3 and I_4 are the intensities of the signals due to styrenyl protons ($\delta(CH_2{=}) = 5.1-5.6$ ppm) and to methoxy protons ($\delta(CH_2OH) = 3.98-3.92$ ppm), respectively. [f] Determined by ^{1}H NMR from the ratio of protons of methylene group ($CH_2{=}/PhCH_2$). [g] $\bar{M}_{n,PEO} = {}^1/_2(44([\text{ethylene oxide}]_0/m)\bar{M}_{n,PS})$ with m = mass of ω-styrenyl PS.

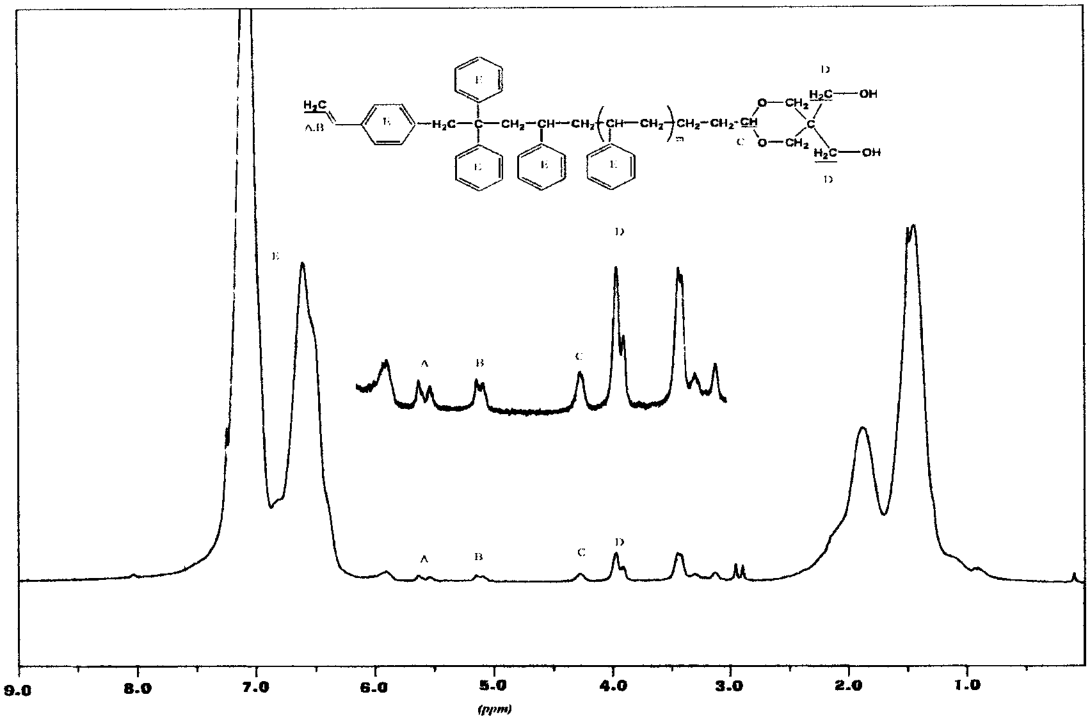


Figure 1. ^{1}H NMR spectrum of **5′** in $CDCl_3$.

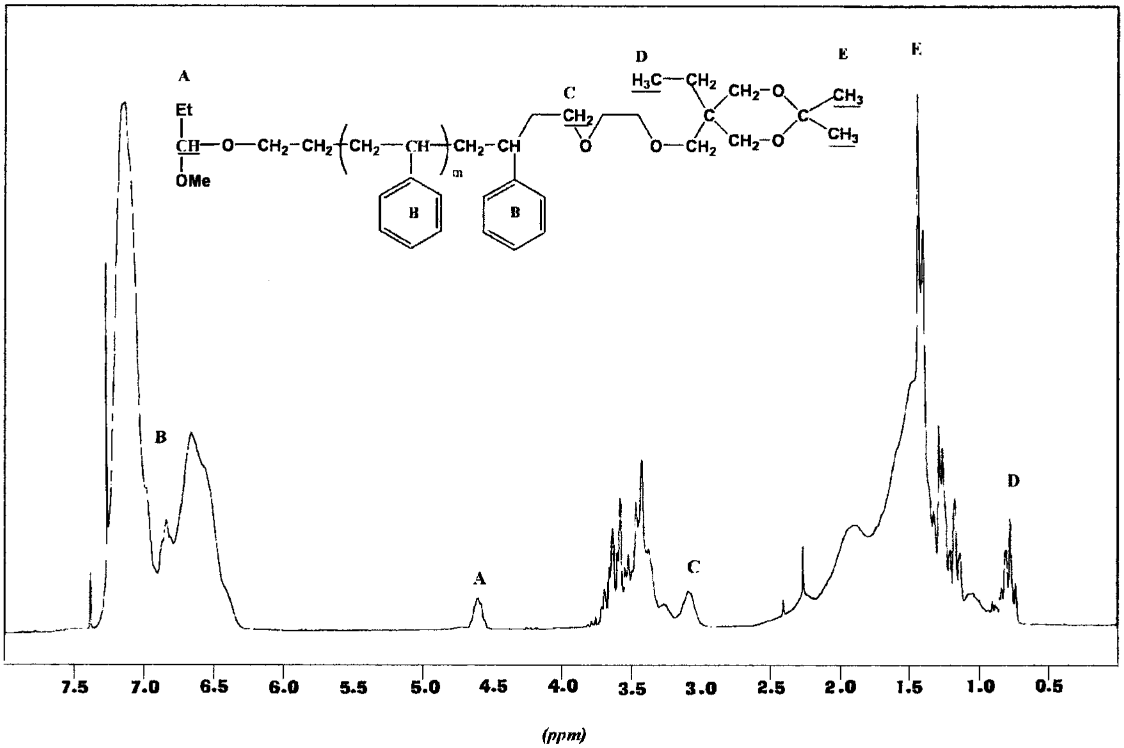


Figure 2. ^{1}H NMR spectrum of **4″** in $CDCl_3$.

Attempts to deactivate carbanionic species with another electrophilic reagent such as **3** were unsuccessful: only 30% of the end-chains could indeed be functionalized. This indicates that the presence of an oxygen atom in the γ-position is essential for chlorine to behave as a good leaving group in agreement with previous observations[22] (Scheme 4). The α-acetal, ω-ketal PS (**4″**) obtained was then subjected to a selective cleavage of its two terminal protecting functions. Using Amberlyst resin, the acetal function in α-position was selectively transformed into a primary hydroxyl as indicated by the complete disappearance from the NMR spectrum of the signal due to the acetal proton at 4.6 ppm; yet the ω-ketal ring could be preserved and further used to introduce a styrenyl unsaturation (**6″**). The ketal ring in ω-position of **6″** was then cleaved by reaction with PTSA, the two hydroxyls generated serving to subsequently grow two PEO blocks.

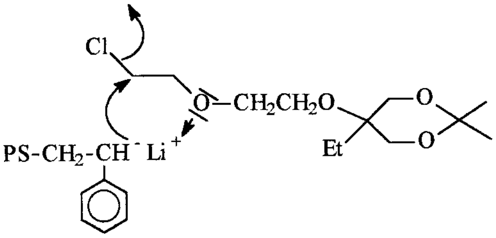
This gemini-shaped PS-*b*-PEO_2 macromonomer was characterized by ^{1}H NMR and SEC. As expected, the

Table 4. Characteristics of PS-*b*-PEO$_2$ Gemini Dispersant Synthesized via Route 2

[styrene]$_0$/ [initiator]$_0$	$\bar{M}_{n,PS}$[a] targeted	$\bar{M}_{n,PS}$ SEC	$\bar{M}_w/\bar{M}_n$ SEC	$\bar{M}_{n,PS}$[b] ^{1}H NMR	(cyclic acetal end/acyclic acetal end)[c]
14	1818	1900	1.12	1560	0.98

[a] Calculated from [([styrene]$_0$/[initiator]$_0$)$M_{styrene}$] + M_{end}, $M_{styrene}$ being the molar mass of the styrene units and M_{end} the molar mass of end groups. [b] Calculating upon taking the ratio of the area of the signal corresponding to the acetal proton (I_1, δ(CH(OEt)Me = 4.6 ppm) to that of the aromatic protons (I_2, δ = 6.2−7.2 ppm): 104(5I_1/I_2). [c] Determined from the ratio of methylene of cyclic acetal (I_1, δ(CH_3CH$_2$) = 0.74−0.85 ppm) to that of acetal proton (I_2, δ(CH(OEt)Me) = 4.6 ppm): I_1/3I_2. [d] Determined from the ratio of the methylene protons of cyclic acetal (I_1, δ(CH_3CH$_2$) = 0.74−0.85 ppm) to those of methylene of styrenyl (I_3, δ(CH_2=) = 5.1−5.6 ppm): 2I_1/3I_3.

Scheme 4. Participation of Oxygen in the Deactivation of Carbanionic Species



size of the PEO corresponded to that targeted and the SEC traces of this copolymer exhibited a narrow molar mass distribution.

Emulsion Polymerization of Styrene in the Presence of PS-*b*-PEO$_2$ Gemini-Type Reactive Surfactant. The emulsion polymerizations of styrene were carried out using the previously described ω-styrenyl PS-*b*-PEO$_2$ gemini-type reactive surfactant, at 60 °C, in a batch reactor. The initiator used was potassium persulfate. To compare the effect on the polymerization kinetics of gemini-type surfactant (G) with that of its linear homologue (L) (same composition, molar mass, and polymerizable unsaturation) two emulsion polymerizations using successively the two macromonomers as dispersant have been carried out under identical experimental conditions.

In Figure 3, the surface activity of these surfactants is shown. Significant differences were observed depending on the type of polymeric surfactants used. The critical micelle concentration (cmc) value on G is slightly higher than the one measured for its linear homologue compound (L), although the two surfactants exhibit approximately the same hydrophilic−hydrophobic balance. This surprising result can be accounted for by the steric effect: PS-*b*-PEO$_2$ macromonomer indeed exhibits a higher steric hindrance than L due to its miktoarm star-shape and therefore requires more energy than L for its associating into micelles. On the other hand, one can also notice that the variation of the surface tension as a function of the concentration is also very different for G and L: the curve representing this evolution actually shows an inflection between two distinct domains of variation for G whereas it exhibits a more continuous variation for L. This may be attributed to existence of best-defined hydrophobic/hydrophilic−water interfaces when the PS-*b*-PEO$_2$ surfactant is used.

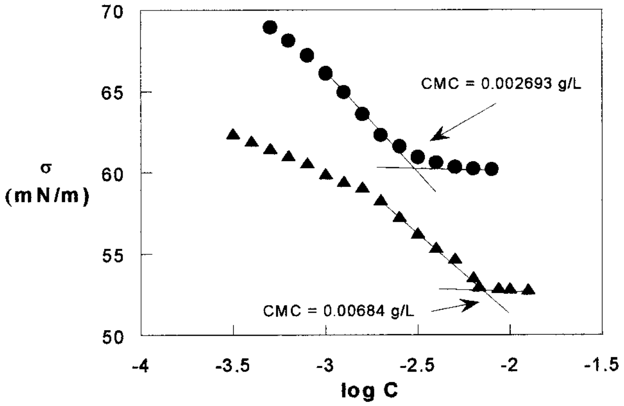


Figure 3. Surface tension vs log(concentration) variation for the (▲) PS-*b*-PEO$_2$ gemini-type and (●) PS-*b*-PEO linear macromonomer surfactants.

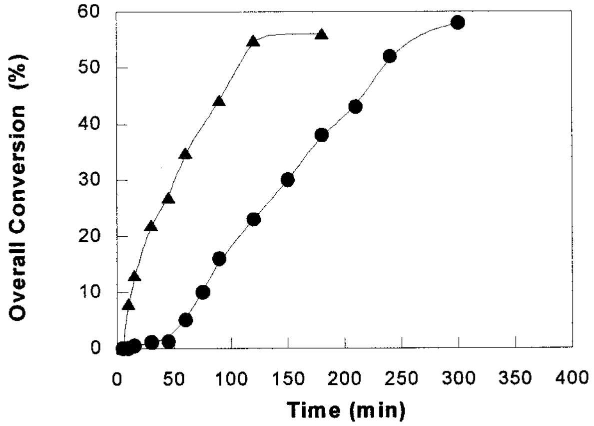


Figure 4. Overall conversion vs time for the emulsion polymerization of styrene using (▲) PS-*b*-PEO$_2$ gemini-type and (●) PS-*b*-PEO linear macromonomer surfactants.

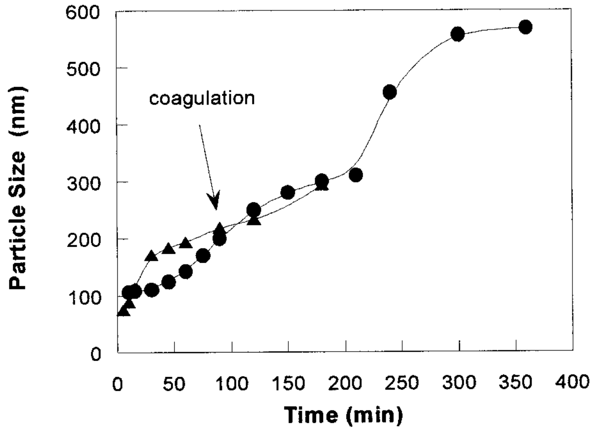


Figure 5. Particle size vs time for the emulsion polymerization of styrene using (▲) PS-*b*-PEO$_2$ gemini-type and (●) PS-*b*-PEO linear macromonomer surfactants.

The overall conversion and the mean particle diameter vs time curves are given in Figures 4 and 5, respectively. For G as for L the final overall conversions were found close to 60%, the conversion curve exhibiting an induction period for the linear surfactant and not for G. Similar retardation effect has previously been reported for polymeric surfactant of high molar mass[9]—due to the difficulty for the monomer, the radicals, or oligo-radicals to diffuse inside the micelle because of steric hindrance. In contrast, no induction period was observed when using the PS-*b*-PEO$_2$ macromonomer as dispersants. This absence of induction period may be due to a faster exchange between the gemini dispersant present in the medium and those engaged in the micelles, which is known to critically depend on the molecular characteristics of the surfactant.[10] The better-defined interface may also explain the easier migration of the monomer inside the micelle.

Whether G or L was used as the surfactant, the medium began to coagulate after about 100 min, but the overall conversion was three times higher for the gemini stabilized particles; in contrast, the particle size was approximately the same whatever the type of dispersant used. This means that the use of gemini-type surfmers resulted in a large number of particles as shown by the kinetic data.

The formation of a coagulum could be explained by the self-association of the reactive surfactants in water and by the high reactivity of the styrenyl entity, leading to their rapid consumption and early incorporation into the particle. Being immobilized in the particles first created, they could not fully play their role of stabilizing agent. In contrast, they could be successfully used in dispersion polymerization, the results obtained being described in a forthcoming publication. One way to slow the rapid consumption of these reactive surfactants in a batch process would be to reduce the reactivity of the terminal unsaturation. The synthesis of new PS-*b*-PEO$_2$ gemini-reactive surfactants functionalized with a maleate group and their use in emulsion polymerization are currently in progress in our laboratory.

Experimental Part

Materials. Styrene was first distilled over CaH$_2$ and stirred over the same drying agent for 24 h before being vacuum distilled. Ethylene oxide was stirred over sodium at −30 °C for 3 h and vacuum distilled. *p*-chloromethylstyrene, 1,1-diphenylethylene, and 3-chloropropionaldehyde diethyl acetal (**1′**) were stored over CaH$_2$ and vacuum distilled. *N*,*N*,*N′*,*N′*-Tetramethylethylenediamine (TMEDA) was stirred over sodium and vacuum distilled. Acetone was stirred over MgSO$_4$ and then freeze vacuum distilled. Amberlyst, CCl$_4$, triphenylphosphine, *p*-toluenesulfonic acid (PTSA), ethylene glycol, pentaerythritol (**4′**), benzyl bromide, dimethylformamide, and 1,1,1-tris(hydroxymethyl)propane (**1**) were used as received. THF, benzene and ether were distilled from sodium−benzophenone. (Diphenylmethyl)potassium,[20] 3-lithiopropionaldehyde diethyl acetal[21] (**2′**), acetaldehyde 3-lithiopropyl ethyl acetal[11] (**2′′**), and 5-ethyl-5-hydroxymethyl-2,2-dimethyl 1,3 dioxane[23] (**2**) were synthesized according to well-established procedures. *p*-Iodomethylstyrene was synthesized in situ from the reaction of *p*-chloromethylstyrene with NaI.

NMR spectra were performed using a Bruker AC200 spectrometer.

Size exclusion chromatography was performed using a JASCO HPLC pump type 880-PU, TOSOHAAS TSK gel columns, a Varian series RI-3 refractive index detector, and a JASCO 875 UV/vis absorption detector with tetrahydrofuran as the mobile phase. Calibration was performed by means of polystyrene standards.

Critical micellar concentrations were determined by looking for the discontinuity on the log(concentration) vs surface tension curve.

Measurements of the surface tension were carried using a KSV Instruments Ltd. tensiometer.

The overall conversions of the polymerization vs the time were determined upon gravimetry determination of the weight of the polymer formed after a given time.

The particle size was determined by photon correlation spectroscopy using a Coulter N4Plus.

Synthesis of 3. The chlorination of **2** was carried out in CCl$_4$ in the presence of PPh$_3$. Typically, into a three-neck flask equipped with a magnetic stirring bar, a reflux condenser and an addition funnel was added 17.4 g (0.1 mol) of **2**. PPh$_3$, 53 g (0.2 mol) dissolved in 200 mL of CCl$_4$, was introduced dropwise under argon onto the reaction medium over a period of 1 h at room temperature. The mixture was then heated to 60 °C for about 24 h. The conversion was followed by gas chromatography and showed a yield close to 99%.

The mixture was then washed and filtered three times with diethyl ether. This organic solution was then concentrated and distilled under vacuum. The colorless product (**3**) was dried over CaH$_2$ and cryodistilled from a sodium mirror to eliminate residual amount of alcohol.

Synthesis of 4. Into a 100 mL two-neck flask, equipped with a magnetic stirring bar, 0.084 of lithium powder was introduced under inert atmosphere. Then 0.014 mol of **3** was dissolved in 15 mL of dried diethyl ether and introduced into the flask containing the lithium and cooled at −30 °C. The medium was left overnight under stirring at −30 °C.

Synthesis of 5: $\bar{M}_{n,targeted}$ = 1535 g/mol. PS living chains were prepared using the lithium initiator **4**.

In a typical reaction, styrene (12.5 g, 13.75 mL, 0.12 mol) was dissolved in 250 mL of solvent. The initiator **4** (0.012 mol), in diethyl ether solution (15 mL), was added at once after filtration of the excess of lithium and salts.

The reaction medium was stirred for 2 h. 1,1-diphenylethylene (4.326 g, 4.237 mL, 0.024 mol) was then added to the medium. After 2 h of reaction the active centers were deactivated by addition of *p*-chloromethylstyrene (5.638 g, 5.250 mL, 0.036 mol). After filtration to remove LiCl salts, precipitation of **5** was performed using methanol.

For the polymerization in benzene a small amount of *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) was added in order to prevent carbanionic species from aggregating in an apolar medium.

Synthesis of 6: $\bar{M}_{n,targeted}$ = 3480 g/mol. A CH$_2$Cl$_2$ solution (400 mL) of the macromonomer **5** (5 g, 0.001 436 mol) was introduced into a 500 mL flask equipped with a magnetic stirring bar. Successively, ethylene glycol (11.173 g, 10.038 mL, 0.180 mol) and PTSA (2 g, 0.0105 mol) were added. The solution was stirred at room temperature for 12 h.

To neutralize the medium and remove the excess of ethylene glycol and other water-soluble compounds, **6** was washed with basic water. The organic solution was then dried over MgSO$_4$, and precipitation using methanol allowed us to isolate **6**.

Synthesis of 7: $\bar{M}_{n,PEO\ targeted}$ = 7000 g/mol. To avoid the presence of water, the α-dihydroxyl, ω-styrene PS macromonomer (3 g, 8.620×10^{-4}mol) was submitted to several freeze-drying in dioxane then dissolved in 150 mL of THF. Quantitative deprotonation of the two hydroxyl groups was performed by slowly adding (diphenylmethyl)potassium in THF (0.71 mol/L, 2.428 mL).

Ethylene oxide (12 g, 13.60 mL, 0.27 mol) was added at 0 °C. After addition of the monomer, reaction medium was stirred for 48 h and the temperature was allow to rise to room temperature. The alkoxide of the PEO chain ends were deactivated with benzyl bromide (0.45 g, 0.313 mL, 2.63×10^{-3}mol) and the block copolymer precipitated in diethyl ether, after removing the KBr salts by filtration.

Synthesis of 3′: $\bar{M}_{n,targeted}$ = 2300 g/mol. This macromonomer was obtained following a previously published method.[21]

Synthesis of 5′: $\bar{M}_{n,targeted}$. A DMF solution (250 mL) of **3′** (1 g, 3.70×10^{-4}mol) was introduced in a 500 mL flask equipped with a magnetic stirring bar. Pentaerythritol (0.51 g, 3.74×10^{-3}mol) was added and after complete dissolution of the compound, a small amount of PTSA (0.5 g, 0.0026 mol) was added to decrease the pH of the medium. After 12 h of mixing at room temperature, CH$_2$Cl$_2$ (250 mL) was added to the organic solution.

To remove DMF and the excess of pentaerythritol and also neutralize the medium the solution was washed with basic water then with pure water. The CH$_2$Cl$_2$ solution was then dried over MgSO$_4$ and after filtration and precipitation in methanol the macromonomer **5′** could be isolated.

Synthesis of 6′: $\bar{M}_{n,PEO\ targeted}$ = 12 150 g/mol. This last step is the same procedure as that described above for the synthesis of the PS-*b*-PEO$_2$ gemini **7**.

Synthesis of 3″. This compound was obtained according to an already published procedure.[24]

Synthesis of 4″: $\bar{M}_{n,targeted} = 1818$ g/mol. The initiation and the growth of polystyrene chains in a benzene solution with TMEDA were already described in a previous work.[11]

The lithiated compound (4.1×10^{-3}mol in 15 mL of dried diethyl ether), obtained from acetaldehyde 3-chloropropyl ethyl acetal (**1″**) was added at once to a benzene solution containing styrene (6.032 g, 6.636 mL, 0.058 mol) and TMEDA (0.720 g, 0.935 mL, 6.21×10^{-3}mol).

The functionalization was carried out by deactivation of the active polystyryl centers with the cyclic acetal **3″** (1.64 g, 6.15×10^{-3}mol). The reaction was stirred for 12 h at room temperature. During this time the red medium, attesting to the presence of polystyryl carbanionic species, became progressively colorless. After filtration of LiCl salt, the polymer **4″** could be isolated by precipitation in methanol.

Synthesis of 5″. The polymer **4″** (5 g, 2.63×10^{-3}mol) was dissolved in a small amount of THF. In a 500 mL flask, equipped with a stirring magnetic bar, acetone (400 mL) and amberlyst resin (6 g) and some drops of water were successively added to the solution of THF. The presence of acetone was essential to preserve the ketal ring in ω-position since it can regenerate the protective ketal ring by reacting with 1,3-diols adventitiously formed. After 12 h of mixing, the organic solution was filtered to remove the excess of resin, neutralized by K_2CO_3 and then precipitated in methanol to give **5″**.

Synthesis of 6″. The use of DPMK involves the absence of any water in the polymer. Therefore, after several freeze-drying in dioxane, **5″** (4 g, 2.10×10^{-3}mol) was deprotonated with DPMK (0.71 mol/L, 2.96 mL). *p*-iodomethylstyrene (2.73×10^{-3}mol) was used as deactivating agent in order to introduce the styrenic double bond. **6″** was isolated by precipitation in methanol after 12 h of reaction at room temperature and removing salts by filtration.

Synthesis of 7″: $\bar{M}_{n,PEOtargeted} = 3800$ g/mol. This reaction follows the same procedure as the one already described.

Emulsion Polymerization. Emulsion polymerizations were carried out in a 1 L jacketed glass reactor fitted with a reflux condenser stainless steel stirrer, sampling device, and nitrogen inlet tube.

In a typical polymerization, the reactor was charged with 1.35 g of PS-*b*-PEO_2 surfactant, 30 g of styrene, 0.4 g of potassium persulfate and 217 mL of water. It was thermostated at 60 °C under vigorous stirring and deoxygenated by bubbling nitrogen through it.

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