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Synthesis, characterization and micelle formation of amphiphilic graft copolymers

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The macromonomer method is a useful tool for the preparation of various graft copolymers with well-defined structure and composition. Macromonomers were prepared by anionic polymerization of styrene followed by a direct coupling reaction of polystyryllithium with an excess of vinylbenzyl chloride. The control of the terminal functional groups is particularly important to ensure the reactivity of macromonomers in the radical copolymerization; the degree of functionality was determined by both n.m.r. and u.v.-vis. spectroscopy to be from 85–99%. Graft copolymers were synthesized by radical copolymerization of (vinylbenzyl) polystyrene macromonomer with 2-hydroxyethyl methacrylate (HEMA), or with acrylic acid. The organization ability of the copolymers to form micelles was investigated by ^{1}H n.m.r. spectroscopy, and verified by their ability to stabilize emulsions. These copolymers were found to be effective surfactants for emulsion polymerization of polystyrene latexes. © 1997 Elsevier Science Ltd.

(Keywords: (vinylbenzyl) polystyrene macromonomer; anionic polymerization; amphiphilic graft copolymers)

INTRODUCTION

The synthesis of macromonomers and their use in the preparation of a variety of graft copolymers has become of interest in recent years[1,2]. These copolymers can exhibit unique morphologies based on microphase-separated structures[3,4]. While some differences in solution properties between graft and block copolymers have been reported[5], the ability of both types of copolymers to form stable micelles in solvents which are selective for one component is generally known (*Figure 1*)[6,7]. Whereas block copolymers[8] as well as amphiphilic macromonomers[9,10] have been used widely as emulsifiers or stabilizers in emulsion or dispersion polymerization, only a few reports deal with the micellization of graft copolymers[11,12].

While micelles are used today for a wide variety of applications such as latexes for synthetic rubber, paints, coatings, adhesives, etc., they are also finding new applications in the biomedical and biotechnological domains as diagnostic tests, immunoassays, or for cell labelling[13].

The interest here is to synthesize two types of amphiphilic graft copolymers, and to show their ability to form stable micelles demonstrating their surfactant properties through the synthesis of polystyrene (PSt) latex particles. PS latexes with a shell containing carboxylic acid units[14] or a shell containing amine groups[15] have been prepared by other researchers.

The comonomers were free-radically copolymerized *in situ* to yield monodisperse PS latex. The copolymers obtained were random and it was difficult to obtain a shell constituted only of functional units. Moreover, the morphology was highly influenced by this procedure and the particles obtained were not spherical. Graft copolymers could represent a satisfactory alternative toward obtaining the core–shell latexes desired and lead to water soluble 'polymeric loops' as stabilizer as compared to diblock copolymers which yield 'hairy-latexes'[8].

The macromononer method for preparing graft copolymers consists of preparing the branches first followed by preparation of the grafted structure through addition between the added monomer and the polymerizable group at the branch ends[16]. Styrene has been anionically polymerized to form (vinylbenzyl) polystyrene macromonomer. Subsequently, this macromonomer has been copolymerized with 2-hydroxyethyl methacrylate (HEMA) and acrylic acid and this has led to the desired graft copolymers. Emulsion polymerization of PS was then carried out in water using these copolymers as surfactants, in order to prove the existence of stable micelles.

EXPERIMENTAL

Material

Solvents used for anionic polymerization were purified by conventional procedures. Tetrahydrofuran (THF) was dried by refluxing in the presence of the benzophenone-sodium complex under a nitrogen atmosphere and was distilled just prior to use. Cyclohexane was distilled

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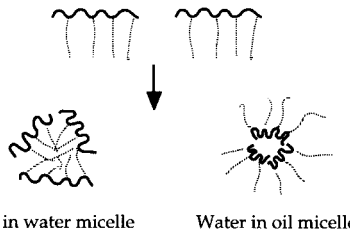


Figure 1 Schematic representation micelles formed by amphiphilic graft copolymers. ——, Hydrophilic polymer backbone; ·····, hydrophobic polymer graft

from sodium under nitrogen. Dimethylformamide (DMF) was distilled from calcium hydride. Other solvents were used as received. Deuterated solvents $CDCl_3$ and CD_3OD (both 99.8% Dr Glaser AG) for proton nuclear magnetic resonance (^{1}H n.m.r.) spectroscopy were used as supplied.

Glassware and syringes were dried prior to use in an oven at 130°C. Styrene and vinylbenzyl chloride, mixture of 3- and 4-isomers (VBC) (Aldrich) were each stirred with calcium hydride for 30 h and vacuum distilled just prior to use. Sec-butyllithium (s-BuLi) (Aldrich) was used as received. 2-Hydroxyethyl methacrylate (HEMA) was distilled from calcium hydride under reduced pressure and acrylic acid was recrystallized just before use.

Macromonomer synthesis

A general procedure for the preparation of macromonomer is given by the following specific example. 5 g (48 mmol) of freshly distilled styrene and degassed cyclohexane (20 ml) were charged via syringe into a 50 ml round bottomed flask equipped with a magnetic stir bar and rubber septum under an argon atmosphere. s-BuLi was slowly added to the stirred mixture until the characteristic colour of the styryl anion was achieved. Once the impurities in the system were thus titrated, 1.92 ml of s-BuLi (0.024 mmol) as initiator was added. Dry and oxygen free THF was subsequently added to the solution in order to accelerate the propagation. The proportion of solvent was 30% of cyclohexane and 60% of THF.

The reaction was allowed to proceed for 1 h at room temperature before the polystyryllithium solution was transferred under a pressure of argon through a cannula to another flask containing VBC in THF (using four- to six-fold excess reagent over s-BuLi). This coupling reaction was carried out for 1 h at 0°C. The macromonomers were then precipitated in 0.5 l of methanol, collected by filtration, and dried under vacuum at room temperature overnight. The material was then extracted with 0.2 l of hot methanol during one night and dried under vacuum at room temperature to constant weight.

Copolymerization reaction

Free-radical copolymerization of the VB–PSt macromonomers with two types of comonomers (HEMA and acrylic acid) was carried out. The macromonomer and the respective comonomer (initial monomer concentration: 15 wt%) were stirred in DMF in sealed tubes (Ace pressure tubes) under argon pressure at 60°C using azobisisobutyronitrile (AIBN) as initiator (2 wt% to total monomer). Copolymers containing HEMA (PSt–HEMA) were precipited into methanol or petroleum ether depending on the amount of hydrophilic monomer (when the copolymer contained mainly HEMA units, the precipitation was done in petroleum ether).

Copolymers with acrylic acid (PSt–AA) were precipitated into methanol only. When the amount of acrylic acid was high, it became difficult to do the precipitation in methanol so the solvent was simply evaporated. Extraction in diethyl ether or hot cyclohexane (50°C) during several hours permitted removal of unreacted macromonomers.

Preparation of polystyrene latex

The latexes were prepared using the following general procedure: styrene (0.1 g), water (3.22 ml) and the graft copolymer (0.02 g) were emulsified using both stirring and ultrasonic irradiation during 40 min. The solution was then transferred under argon atmosphere to a tube which was sealed after the addition of 1.5 mg of AIBN. The reaction was then allowed to proceed for 8 h at 60°C followed by cooling the tube to 0°C before characterization was performed.

Measurement and characterization

^{1}H n.m.r. spectra were recorded on a Bruker ACP-200 operating at 200 MHz. Gel permeation chromatography (g.p.c.) was performed on a HPLC Kontron system (with u.v. detector) equipped with ultrastyragel columns ($10^5 + 10^4 + 10^3$ Å) and calibrated with standard polystyrene samples. The eluent [THF or a mixture of dichloromethane with 3% of hexafluoroisopropanol (HFIP)] was used at a flow rate of 1 ml min^{-1}. U.v.-visible (u.v.-vis.) spectra were obtained from a Lambda 6 UV-Vis spectrometer (Perkin–Elmer) in quartz cells with THF as solvent.

Quantitative analysis of vinylbenzyl end-groups was carried out using PSt, (vinylbenzyl) polystyrene macromonomer (VB–PSt), and *p*-methylstyrene (*p*-MS) with the respective concentrations at 4.022, 4.106, and 0.146 g l^{-1}.

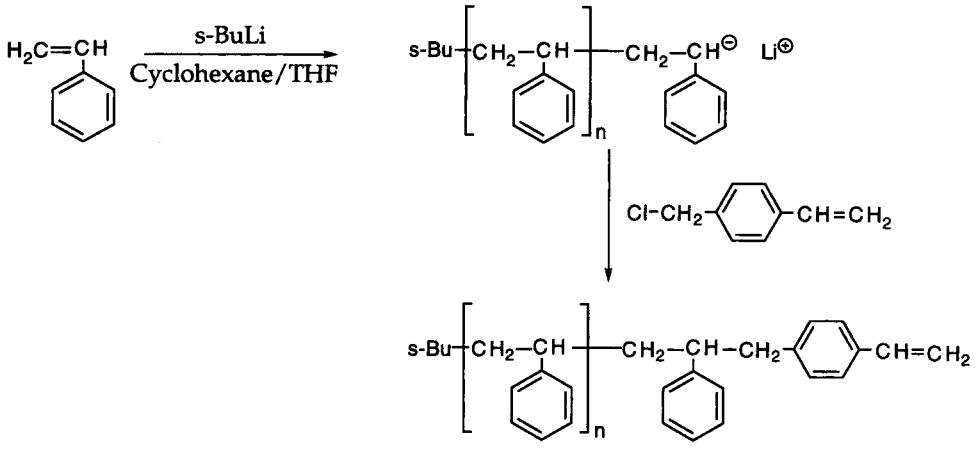
Transmission electron microscopy (TEM) photographs were obtained using a Philips EM 300 at 100 kV. Samples were prepared by placing a small drop of the latex solution onto a carbon grid. Water was allowed to evaporate at room temperature before analysis.

RESULTS AND DISCUSSION

Macromonomer preparation

In order to have well-defined grafts in the copolymer surfactant, living anionic polymerization was utilized for their preparation. The general reaction is depicted in *Scheme 1*. (Vinylbenzyl) polystyrene (VB–PSt) macromonomer was synthesized in a mixed solvent of cyclohexane and THF. Polystyryllithium (PSt–Li) was prepared in a round bottom flask under argon atmosphere using syringe techniques, while the functionalization was performed by the addition of the PSt–Li to the VBC in THF. The characteristics of the afforded macromonomers are given in *Table 1*. Yields were quantitative and the number average molecular weights, ranging from 2090 to 3515 g mol^{-1}, were close to that expected for the molar ratio of the monomer to the initiator.

G.p.c. spectra of the macromonomers obtained show a narrow molecular weight distribution with only a small shoulder in the higher mass region (*Figure 2*). Asami *et al.*



Scheme 1 Vinylbenzyl polystyrene macromonomer synthesis

showed this reaction could lead to some extent of side reaction forming dimeric-terminated polystyrene by a one-electron-transfer mechanism[17]. It is suggested that it is possible to minimize this side reaction by using a mixed solvent of hydrocarbon with enough aprotic polar solvent such as THF. Reactions such as that shown in *Scheme 2* are also possible in this reaction and are most likely the cause of the high molecular weight shoulder. The presence of the small shoulder in the g.p.c. spectrum corresponding to exactly twice the molecular weight of the macromonomer indicates that a small amount of dimers were thus produced. This small amount of dimeric product was considered negligible and it did not constitute a problem for graft copolymer synthesis as shown in the next section.

The analysis of the initially precipitated macromonomer by ^{1}H n.m.r.spectroscopy showed that VBC was still present in the polymer even after precipitation in methanol. *Figure 3* confirms this presence by superposition of the macromonomer spectrum with that of

Table 1 Characterization of (*p*-vinylbenzyl) polystyrene macromonomers

Run	M^a theoretical	M_n g.p.c.	M_w/M_n g.p.c.	VB–PSt% u.v.	VB–PSt% n.m.r.
M-1	2000	2110	1.12	91	88
M-2	2000	2090	1.10	87	85
M-3	3500	3515	1.05	99	99

[a] M (g mol^{-1}) are calculated from the mole ratio of monomer to initiator

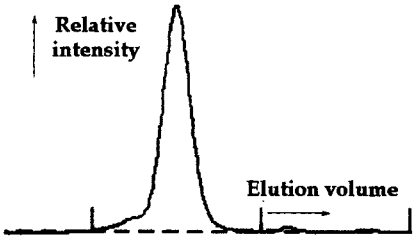


Figure 2 G.p.c. spectrum of polystyrene macromonomer

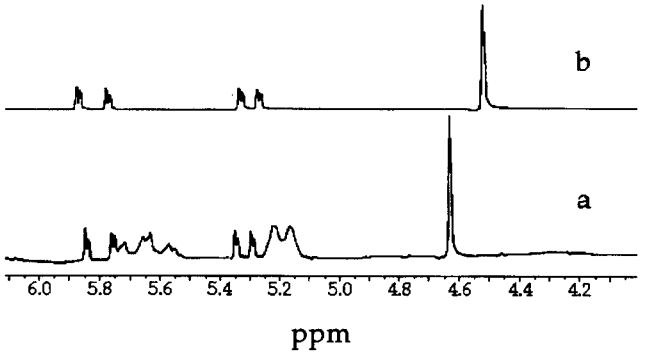
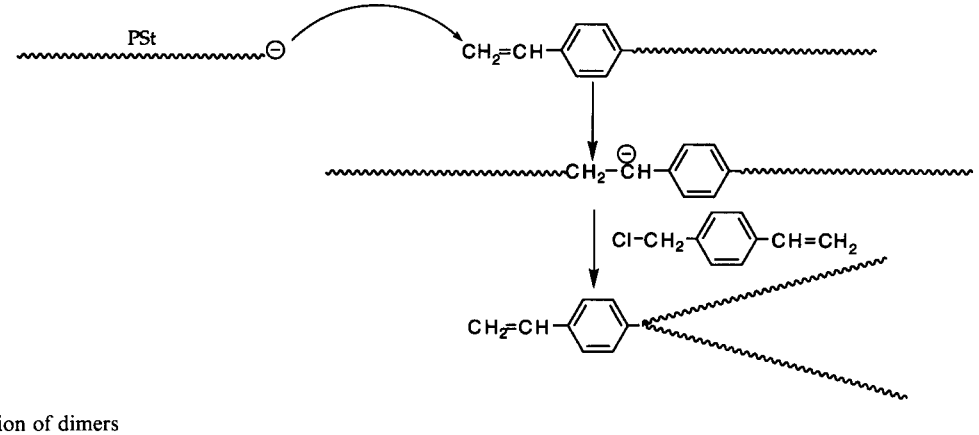


Figure 3 Dual display of spectra showing olefinic and benzylic peaks; (a) polystyrene macromonomer spectrum; (b) vinylbenzyl chloride spectrum



Scheme 2 Formation of dimers

VBC; the matching between the peaks of both spectra is obvious. However, extraction in hot methanol during one night eliminated the VBC contamination and ensured the macromonomer purity. The degree of functionalization was investigated both by ^{1}H n.m.r. and u.v.-vis. spectroscopy (*Figures 4* and *5*). In order to increase the sensitivity, ^{1}H n.m.r. spectra were obtained after long acquisition times (about 16 000 scans).

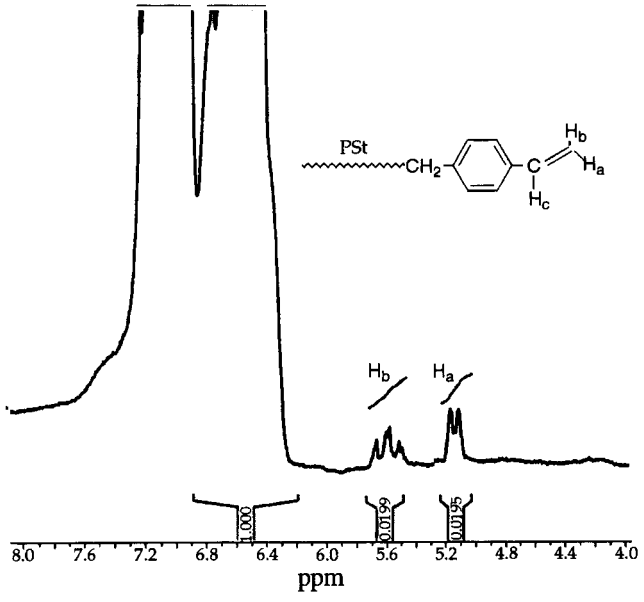


Figure 4 ^{1}H n.m.r. spectrum of the styryl end functionality of the polystyrene macromonomer

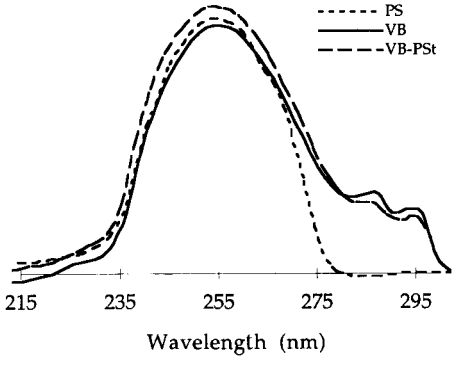


Figure 5 U.v. spectra of polystyrene (PS), (vinyl benzyl) polystyrene macromonomers (VB–PSt), and *p*-methylstyrene (VB) as a model compound

The ^{1}H n.m.r. spectrum in *Figure 4* shows peaks at δ 5.1 (*d*; H_a) and δ 5.6 (*m*; H_b); H_c has a shift at lower field so the expected quadruplet is hidden by peaks due to the aromatic protons of polystyrene. The multiplet obtained for H_b is assumed to be due to the isomeric mixture of the VBC utilized. The peaks corresponding to H_a and H_b show a similar integration value and the ratio of that value with the integration value of polystyrene aromatic peaks yields the number average molar mass (M_n). The comparison of the value of M_n with that obtained by g.p.c. gives the degree of functionalization.

The values given by ^{1}H n.m.r. were confirmed by u.v.-vis. spectroscopy. *Figure 5* shows u.v. spectra of VB–PSt, *p*-methylstyrene (used as reference) and polystyrene. The spectrum of VB–PSt has a λ_{max} at 260 nm in THF and is similar to a resultant spectrum of polystyrene and *p*-methylstyrene. The extinction coefficient at 284 nm is calculated from the absorbance of *p*-methylstyrene and the concentration of double bonds in VB–PSt is then deduced. Both methods correspond well and show 99% functionalization for the last sample (*Table 1*) indicating that polystyrene macromonomers obtained are of high purity.

Graft copolymers

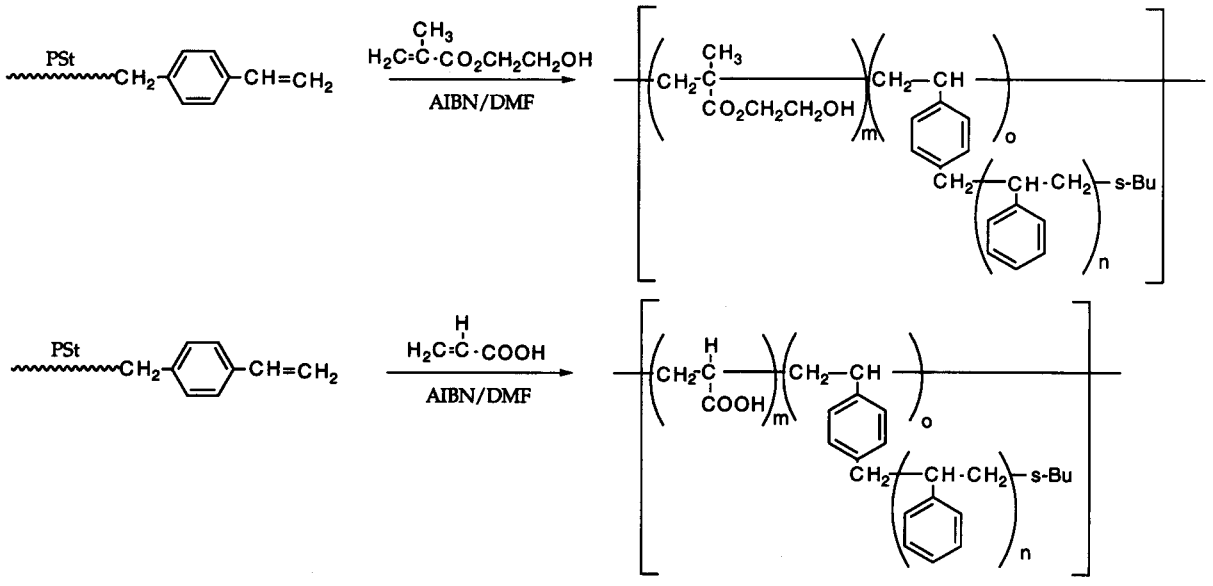
Scheme 3 depicts the reaction scheme for the preparation of graft copolymers. Two types of graft copolymers were obtained here. Polystyrene macromonomers were copolymerized with HEMA or acrylic acid using various amounts of macromonomers with the results summarized in *Table 2*.

The presence of homopolymers (unreacted macromonomers, dimers, HEMA or acrylic acid homopolymers) was eliminated by extraction with suitable solvents. Their removal could be verified by g.p.c. The reactivity of dimers in the free-radical copolymerization might be somewhat lower because of steric hindrance.

When incorporated, however, dimers should not disturb the structure of the graft copolymer as the chain length of the branches would remain the same. However, in the case of PSt–AA copolymers when the amount of acrylic acid was high, it became difficult to do the precipitation in methanol so the solvent was removed by evaporation. Therefore, the presence of poly(acrylic acid) homopolymer could not be avoided; this is not

Table 2 Characteristics of PSt macromonomers, M_1 copolymerized with HEMA or acrylic acid (AA), M_2

Run	M_2 in feed	M_1 in feed			M_1 in polymer n.m.r.		$M_n \times 10^4$ g.p.c.	M_w/M_n g.p.c.
		Sample	wt%	mol%	wt%	mol%		
G-13	HEMA	M-1	33	3.0	28	2.3	1.32	2.48
G-31	HEMA	M-2	50	5.5	43	4.5	3.24	2.51
G-32	HEMA	M-2	66	10.5	60	10	3.16	2.42
G-33	HEMA	M-2	72	13.5	68	13.3	3.09	2.22
G-41	AA	M-3	75	5.8	72.5	5.1	5.6	3.31
G-42	AA	M-3	70	4.6	65	3.5	3.1	2.83
G-43	AA	M-3	50	2	49	1.8	4.2	3.45
G-44	AA	M-3	30	0.9	26	0.7	4.9	3.09
G-45	AA	M-3	25	0.7	24	0.65	4.5	2.78



Scheme 3 Amphiphilic graft copolymer synthesis using HEMA or acrylic acid; *m*, *n*, *o* represent the number of units

really a problem for the preparation of latex particles, since poly(acrylic acid) chains will be dissolved in the aqueous phase.

Free-radical copolymerization does not permit a control of the reaction in such a way as anionic polymerization and it leads to statistical distributions in composition, sequence length, and in molecular weight as given by g.p.c. analysis. However, since g.p.c. results depend not only on molecular weight but also on composition (the retention volume is a function of the hydrodynamic dimension of the polymer in the eluent), the values given here should be considered only as qualitative information.

Chemical composition of the graft copolymers have been calculated from ^{1}H n.m.r. spectra in $CDCl_3$–CD_3OD mixed solvents. For PSt–HEMA copolymers, the relative intensities of the peaks due to phenyl and ester methylene protons observed at δ 6.6–7.1 and δ 3.8–4.1 respectively (*Figure 6*) were used.

For PSt-AA copolymers, the relative intensities used were those of peaks corresponding to aromatic protons (δ 6.6–7.1) and the methine proton at δ 2.45 (=HOOC–C<u>H</u>–) (*Figure 7*).

Radical copolymerization of the macromonomers is greatly influenced by the macromonomer chain length, the molar ratio, the total concentration, and the solvent. Several kinetic studies have been carried out for other macromonomer/comonomer systems[18,19]. Generally, it is difficult to evaluate the macromonomer reactivity ratio. No studies of the copolymerization kinetics were done here to account for the composition of the graft copolymers. The reason for this is that the copolymerization had to be performed at a very high molar ratio of the comonomer to the high molecular weight of the macromonomer so that the copolymer could be satisfactorily analysed by conventional methods. Also, a very important complication is the incompatibility of the macromonomer chain and the backbone which may lead to preferential solvation or even to microphase separation. In this case, it becomes difficult to follow the reaction by n.m.r. analysis or g.p.c. where micelle formation could prevent the measurement (see later). Nevertheless, in some cases, it has been possible to carry out these studies and to

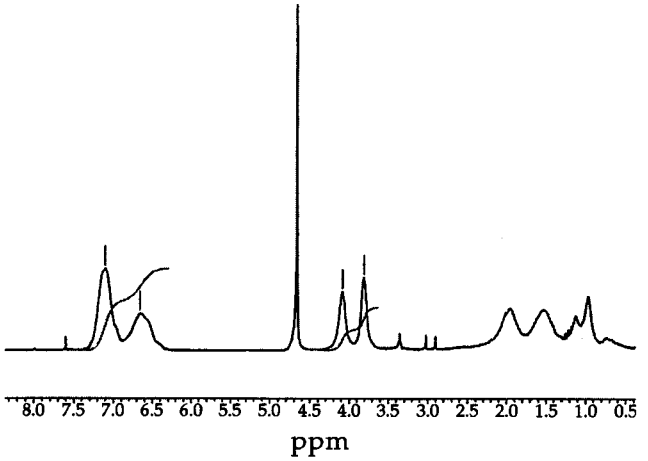


Figure 6 ^{1}H n.m.r. spectrum of PSt-HEMA copolymers (sample G-32) in $CDCl_3/CD_3OD$ (80/20)

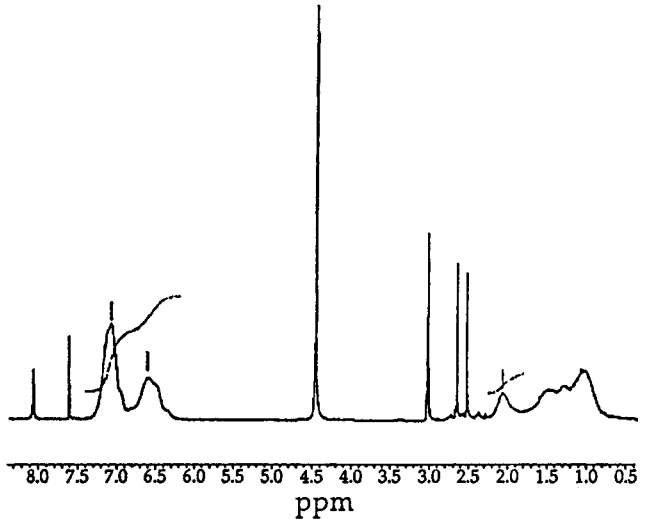


Figure 7 ^{1}H n.m.r. spectrum of PSt–AA copolymers (sample G-43) in $CDCl_3/CD_3OD$ (80/20)

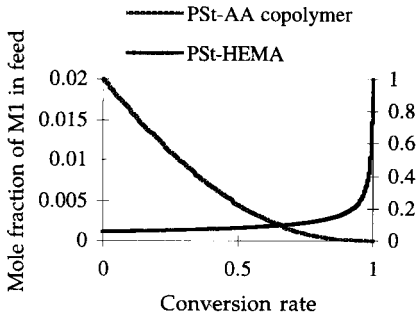


Figure 8 Composition drift of graft copolymers

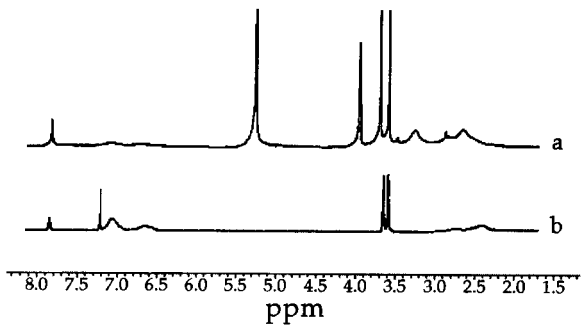


Figure 9 Characterization of micelles by ^{1}H n.m.r.; PSt–AA (sample G-43) in: (a) CD_3OD and (b) $CDCl_3$ only

determine the copolymerization reactivity ratio for certain macromonomer/comonomer systems and it was found that the values are often close to that obtained with simple monomers of similar structure[20,21].

The theoretical reactivity ratio of styrene and HEMA values calculated from the Alfrey-Price Q and e values are respectively $r_1 = 0.4$ and $r_2 = 2.1$, whereas those of styrene and acrylic acid are $r_1 = 0.3$ and $r_2 = 0.2$. This gives information about the expected composition for the corresponding copolymers are shown in *Figure 8*. This figure represents the consumption of the macromonomers (M_1) vs. the conversion rate. In the case of PSt–HEMA copolymer, the polymerization of HEMA is favoured, so it is expected that the initially formed chains consist mostly of HEMA while the chains formed at high monomer conversion are rich in macromonomer. Conversely, for PSt–AA copolymers, alternating copolymerization is favoured and hence the initially formed chains should contain more macromonomer than the chains produced at high conversions. These are only qualitative assumptions, but they give an indication about the probable compositional heterogeneity of the graft copolymers obtained. Of course, more direct evidence could be obtained by arresting the reaction at various degrees of conversion followed by a compositional analysis[19].

Micelle formation and characterization

Block copolymers with these components have been studied[22,23], but the capacity of the corresponding amphiphilic graft copolymers to form micelles in selective solvents or their potential for use as polymeric stabilizers is not well-known. ^{1}H n.m.r. spectroscopy can be used to investigate the micelle formation of these copolymers. This method has previously been used for the characterization of micelles formed from PSt–HEMA copolymers[18].

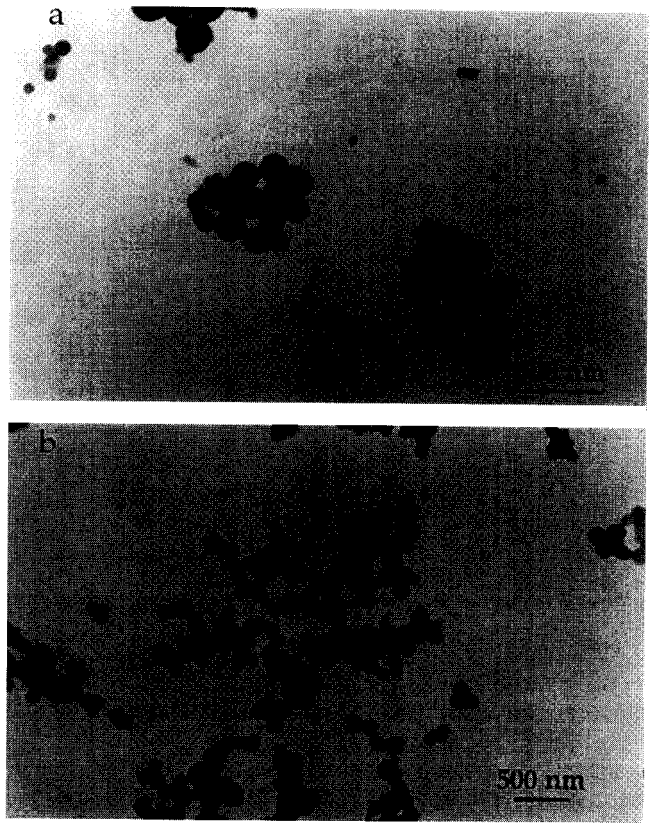


Figure 10 TEM micrographs of polystyrene latex using: (a) PSt–AA copolymers, (b) PSt–HEMA copolymers

These copolymers were formed similarly to the graft copolymers in this paper, except that the precursor macromonomer contained methacrylic rather than vinylbenzylic end groups.

Figure 1 shows the expected conformation of the micelles. In aqueous media, PSt branches constitute the core of the micelle, whereas the shell is comprised of the poly(acrylic acid) (PAA) backbone. In chloroform, or in other organic solvents, the micelle cores are formed by PAA and surrounded by PSt chains. The component which is less soluble in the particular solvent will form the core of the micelle and the corresponding peaks will be too broad to appear in the ^{1}H n.m.r. spectrum due to extensive magnetic dipole interactions. *Figure 9* shows the results obtained with PSt–AA copolymers when the spectra are taken with CD_3OD or $CDCl_3$ only. The characteristic methine peak of PAA at δ 2.45 (=HOOC–C<u>H</u>–) does not appear when $CDCl_3$ is used as the solvent, whereas the peaks due to phenyl protons (PSt) at δ 6.6–7.1 are absent if CD_3OD is the unique solvent. When a mixture of solvents is used, dissolving both blocks as in *Figure 7*, there is no micelle formation and both components appear in the spectrum.

Some g.p.c. analyses were performed in a solvent (dichloromethane with 3% of HFIP) which was only a good solvent for the polystyrene part of the copolymer but not for the PAA part yielding a micellar structure in solution. The molecular weight relative to linear PSt standards corresponds to 8×10^8, whereas the value in THF (solvent for both components of the copolymer) is 5.6×10^4.

This is characteristic of the formation of micelles, and the value of molecular weight given in the first solvent is likely to be an agglomerate of several copolymer chains

forming the micelle. It is important to note that the conformation of the graft copolymers is not as simple as that of block copolymers and the arrangement of copolymer chains forming the micelle could be quite complicated, especially considering the variation in chemical composition of the copolymers.

The formation of micelles as well as the surfactant properties of the copolymers could also be verified through usual emulsion polymerization. Thus, the graft copolymers obtained have subsequently been used for stabilizing the aqueous emulsion polymerization of styrene. The procedure used for the preparation of the latex particles included the stabilizer as a part of the latex recipe (added before polymerization). All of the components (styrene, water, and graft copolymer) were emulsified ultrasonically prior to polymerization. Emulsion polymerization has been carried out using PSt–AA or PSt–HEMA copolymers containing the same amount of each component. It is obvious that stabilizing efficiency of the surfactant in aqueous solution requires a rather high hydrophilic character, but if this hydrophilic character is too high, it may lead to a water soluble copolymer and ultimately to the flocculation of the latex. In order to limit this result, the graft copolymer should have a true amphiphilic structure, i.e. a similar amount of acrylic acid units and styrene units. The particles obtained were characterized by TEM. As expected, the micrographs show that only graft copolymers containing PSt and PAA lead to PS latex particles with well-defined morphology (*Figure 10*).

The PS latex particles obtained with PSt–HEMA were not satisfactory. After some time of emulsion polymerization, the particles were rather sticky. TEM micrographs show that they were neither well defined nor well separated. This can be explained by the fact that PHEMA is hydrophilic but only partially water-soluble and it swells in the presence of water; hence, instead of the steric repulsion necessary for the stabilization, copolymers containing PHEMA should be more or less attracted to each other.

CONCLUSIONS

This study investigated two types of graft copolymers having hydrophilic and hydrophobic sequences, obtained from the copolymerization of (vinylbenzyl) polystyrene macromonomers with HEMA (PSt–HEMA) or acrylic acid (PSt–AA). Macromonomers have been synthesized by anionic polymerization of styrene followed by the coupling reaction with VBC. ^{1}H n.m.r. and u.v. spectroscopy were used to characterize the macromonomers, showing high degrees of functionalization with a small amount of dimeric product. ^{1}H n.m.r. gives evidence of the micelle formation of copolymers in selective solvents. In methanol, polystyrene macromonomer branches form the core of the micelles, whereas the shell is formed by the hydrophilic backbone. PSt–AA copolymers were shown to be efficient as stabilizers in aqueous emulsion polymerization of latex particles, whereas PSt–HEMA copolymers yielded agglomerated particles. In chloroform, inverse micelles are formed and should therefore also function as a stabilizer for dispersion polymerization.

This type of micelle could also be used in the formation and the stabilization of metal nanoparticles which could be formed in the micellar core in an organic solvent. Such investigations are currently in progress in our laboratory.

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