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Amphiphilic Block Copolymers Prepared via Controlled Radical Polymerization as Surfactants for Emulsion Polymerization

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SUMMARY : Amphiphilic block copolymers were synthesized by controlled radical polymerization using either atom transfer radical polymerization (ATRP) or a nitroxide-mediated technique. Those copolymers have a hydrophobic block which is composed of polystyrene and a polyelectrolyte hydrophilic block which is either anionic (poly(acrylic acid)) or cationic (poly(vinylbenzyltriethyl ammonium chloride)). They proved to be efficient stabilizers in the free-radical emulsion polymerization of styrene.

Introduction

It has already been shown that amphiphilic block copolymers can be used as surfactants to stabilize polymer dispersions[1-6]. They are expected to present some advantages over conventional low molecular weight surfactants owing to their better compatibility with the polymer particles and to a lower migration rate. They provide steric stabilization owing to the formation of a hydrophilic shell surrounding the particles and when the hydrophilic segment is a polyelectrolyte, they also provide electrostatic stabilization. Combination of both effects is known as electrosteric stabilization. Until now, well-defined amphiphilic block copolymers were usually synthesized using anionic or cationic "living" polymerizations[1]. However, those techniques require very drastic experimental conditions and a new trend is to replace them by controlled radical polymerization. This method enables to apply radical polymerization to the synthesis of (co)polymers with controlled molar mass, narrow molar mass distribution and well-defined architectures[7]. Control is based on an equilibrium between the active

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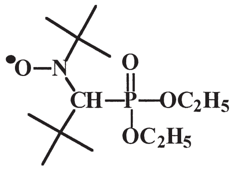
macromolecular radical and a dormant covalent counterpart which is an alkoxyamine in nitroxide-mediated polymerization and an alkyl halide in ATRP. In the case of nitroxide-mediated polymerization, the alkoxyamines undergo thermal reversible activation, while in ATRP a transition metal catalyst complex is needed to provide the reversible activation of the halide terminated dormant chains. TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) is the most widely used nitroxide and was mainly applied for the controlled polymerization of styrenic monomers at T > 120 °C. More recently, a phosphonylated nitroxide stable radical provided by Elf-Atochem, the N-*tert*-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, Scheme 1) was reported to give excellent results in the controlled radical polymerization of styrene and acrylic esters[8].

Scheme 1



In the present work, the copper-mediated ATRP was chosen to synthesize poly(*tert*-butyl acrylate-b-styrene) in order to obtain amphiphilic block copolymers after hydrolysis of the ester groups. The SG1-mediated polymerization was used to synthesize poly(vinylbenzyl chloride-b-styrene) which led to poly(vinylbenzyltriethylammonium chloride-b-styrene) amphiphilic block copolymers after quaternization with triethylamine. Those amphiphilic block copolymers were tested as stabilizers in the free-radical emulsion polymerization of styrene.

Experimental part

Materials. Styrene (St, Acros, 99%) and *tert*-butylacrylate (*t*BuA, Aldrich, 98%) were vacuum distilled over calcium hydride and stored under nitrogen atmosphere at -15 °C. Vinylbenzyl chloride (VBC, Aldrich, 90%), N,N-dimethylformamide (DMF, Acros, 99+%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), copper (I) bromide (CuBr, Aldrich, 99.999%), ethyl 2-bromoisobutyrate (2-EBiB, Aldrich, 98%), trifluoroacetic acid (TFA, Aldrich, 99%), triethylamine (Aldrich, 99%) were used as received.

$NaHCO_3$, $K_2S_2O_8$ and 2,2'-azobis-(2-amidinopropane) dihydrochloride (V50) were obtained from Aldrich and used without further purification.

Analytical Techniques. Molar masses and molar mass distributions were measured by size exclusion chromatography (SEC) in tetrahydrofuran eluent with a set of 10^4, 10^3, 500 and 100 Å microstyragel columns and a refractometric detector, using polystyrene standards. Proton NMR analysis of the polymers was performed at room temperature using a 200 MHz AC200 Bruker spectrometer.

Synthesis of poly(acrylic acid-b-styrene) (poly(AA-b-St)) (A). Polymerizations were performed in sealed tubes after preparation of the reaction mixtures in a glove box. The initiator, 2-EBiB, was added last into the stirred mixture of monomer, CuBr, PMDETA and DMF. The homogeneous solutions were deoxygenated under vacuum by freeze-thaw cycles. After being sealed off, the tubes were immersed in a thermostated oil bath for polymerization. The obtained polymers were isolated by evaporation of DMF and of the unreacted volatile compounds. Conversions were measured by gravimetry after drying the polymer in a vacuum oven at 50 °C. Before SEC analysis, metal catalyst was removed by passing a THF solution of the polymers over a column of activated basic alumina.

Synthesis of poly(vinylbenzyltriethylammonium chloride-b-styrene) (poly(VBTC-b-St)) (B). Polymerizations were performed in bulk in a three-neck flask equipped with a reflux condenser. The mixtures of initiator, monomer and nitroxide (SG1) were bubbled with nitrogen before heating at 120 °C. After reaction, the polymers were recovered by precipitation into methanol.

Emulsion polymerizations of styrene. Batch emulsion polymerizations were carried out in a 100 mL round bottom flask equipped with a reflux condenser and immersed in a thermoregulated oil bath at 70 °C. Deionized water, $NaHCO_3$, the block copolymer stabilizer and styrene were introduced and the emulsion was bubbled with nitrogen. Afterwards an aqueous solution of the initiator ($K_2S_2O_8$ or V50) was added to start the polymerization (time zero). Samples were withdrawn at different time intervals in order to follow the conversion by gravimetry and the particles diameter by dynamic light scattering (Zetasizer 4 from Malvern).

Results and discussion

Synthesis of poly(acrylic acid-b-styrene) (poly(AA-b-St)) (A).

ATRP was shown to be unsuccessful for the polymerization of acrylic acid since side reactions between the monomer and the Cu(II) deactivator occur$^{9)}$. Therefore, *tert*-butyl acrylate monomer was chosen due to its easy hydrolysis into acrylic acid. Low molar mass poly(*t*BuA-b-St) was synthesized by copper-catalyzed ATRP in the presence of DMF, using PMDETA as the ligand. PMDETA, a commercially available multidentate amine, was shown to give fast controlled polymerization$^{10)}$ and DMF to be an efficient additive to homogenize the system$^{11)}$. The method chosen to obtain low molar mass poly(*t*BuA) was to carry out polymerization up to high conversion with a low monomer to initiator ratio. After 3 hours at 50 °C, a system composed of *t*BuA / 2-EBiB / CuBr / PMDETA : 30 / 1 / 0.3 / 0.3 in 25 vol.% DMF yielded 95 % of poly(*t*BuA) with the expected molar mass ($M_{n,\ exp}$ = 3600 g/mol and $M_{n,\ calc}$ = 3640 g/mol) and a low polydispersity (M_w/M_n = 1.08). The isolated polymer was further used as a macroinitiator for the ATRP of styrene at 90 °C using St / macroinitiator / CuBr / PMDETA : 110 / 1 / 0.3 / 0.3 in 25 vol.% DMF. After a reaction time of 2 hours, the experimental molar mass was $M_{n,\ exp}$ = 4600 g/mol. The expected increase of molar mass without any significant increase of polydispersity (M_w/M_n = 1.09) indicates that effective initiation of styrene has taken place. The poly(*t*BuA) block was easily hydrolyzed into poly(acrylic acid) using TFA catalyst in dichloromethane at room temperature for 24 hours. The hydrolyzed copolymer (Table 1) which precipitated in dichloromethane was separated by filtration, washed with the same solvent and dried under vacuum at 50 °C. The degree of hydrolysis (100 %) was calculated by ^{1}H NMR with the disappearance of the resonance at 1.41 ppm (protons of the *tert*-butyl group) and the appearance of the resonance at 12.23 ppm (proton of the carboxyl group).

Synthesis of poly(vinylbenzyltriethylammonium chloride-b-styrene) (poly(VBTC-b-St)) (B).

The synthesis of poly(VBC-b-St) block copolymers using TEMPO-mediated radical polymerization has already been published$^{12,13)}$. In this work, synthesis of the block copolymer was performed by a two-step radical polymerization of VBC and styrene controlled by SG1, followed by quaternization of the first block with triethylamine. The bulk polymerization of VBC initiated by AIBN (0.044 mol/L) and controlled by SG1 (0.103 mol/L) yielded a homopolymer with M_n = 5600 g/mol (M_w/M_n = 1.28) after 45 minutes at 120 °C. This homopolymer was isolated by precipitation into methanol, dried and further used as a macroinitiator (0.018 mol/L) for the bulk polymerization of styrene in the presence of a small amount of free SG1 (to avoid the initially favored irreversible termination reactions) at 120 °C during 45 minutes. The reaction led to a block copolymer (M_n = 6100 g/mol and M_w/M_n = 1.30). The poly(VBC) block was quaternized with excess triethylamine in chloroform at room temperature during 24 hours. The degree of quaternization (69 %) was calculated using proton NMR analysis, with the appearance of the resonance at 3.2 ppm characteristic of the protons of the methylene of the ethyl substituents $N(C\underline{H}_2\text{-}CH_3)_3$ (Table 1).

Table 1. Characteristics of the amphiphilic block copolymers (^{1}H NMR)

Copolymer	Hydrophobic block		Hydrophilic block		
	nature	DP	nature	DP	% chemical modification
A	St	15	AA	28	100
B	St	8	VBTC	34*	69

* taking all the units into account (VBTC + non quaternized VBC)

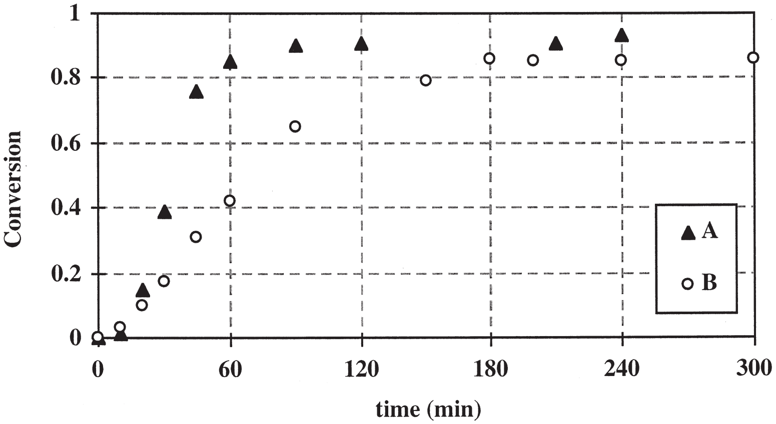


Fig. 1. Conversion versus time for the emulsion polymerizations of styrene at 70 °C
(A) Water (50 g), $NaHCO_3$ (0.05 g ; 1.2 10^{-2} mol/L_{aq}), poly(AA_{28}-b-St_{15}) (0.05 g ; 2.2 10^{-4} mol/L_{aq}), St (5 g), $K_2S_2O_8$ (0.05 g ; 3.7 10^{-3} mol/L_{aq})
(B) Water (20 g), poly($VBTC_{34}$-b-St_8) (0.022 g ; 1.8 10^{-4} mol/L_{aq}), St (2.22 g), V50 (0.0155 g ; 2.8 10^{-3} mol/L_{aq})

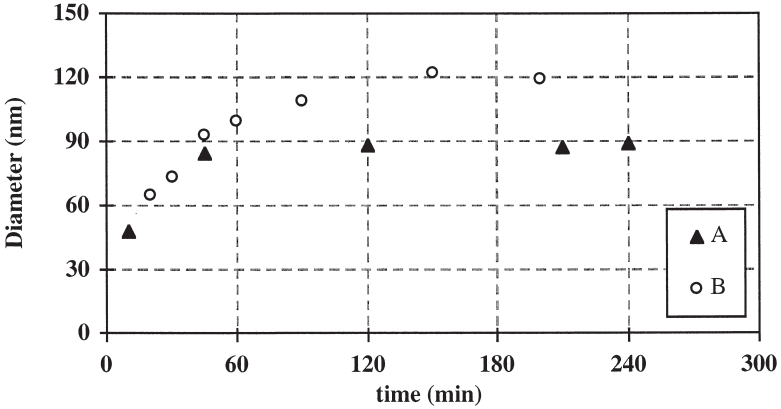


Fig. 2. Particles diameter versus time for the emulsion polymerizations of styrene

Emulsion polymerization of styrene.

The amphiphilic block copolymers were tested as stabilizers in the free-radical emulsion polymerization of styrene. They proved to be powerful electrosteric stabilizers, resulting in particles with small diameter and stable latexes. Results are shown in Figures 1 and 2 (conversion and diameter versus time).

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