Well-Defined Amphiphilic Block Copolymer Nanoobjects via Nitroxide-Mediated Emulsion Polymerization

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S Supporting Information
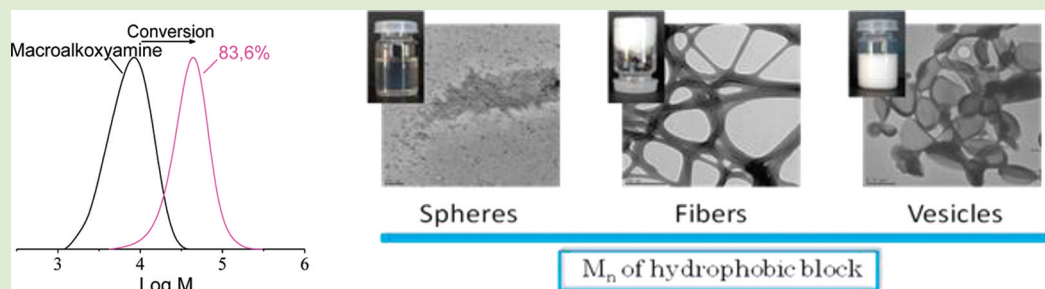
ABSTRACT: Water-soluble macroalkoxyamines are shown to be particularly well-suited initiators for nitroxide-mediated emulsion polymerization. They lead to the synthesis of amphiphilic block copolymers that self-assemble in situ into well-defined nanoobject morphologies, in agreement with the principles of polymerization-induced micellization. Depending on the molar mass of the hydrophobic block, the formed nanoparticles are hairy spherical micelles, nanofibers, or vesicles. The nanofibers are the most intriguing and spectacular structure and strongly affect the physicochemical properties of the aqueous dispersions.

The present paper aims at using the controlled radical polymerization (CRP) method[1,2] based on nitroxide-mediated polymerization (NMP)[3] under emulsion conditions for the elaboration of a variety of amphiphilic nano-objects. Since its discovery, NMP has received a continuous interest from the scientific community and allowed the development of a series of new copolymers and new materials in very simple experimental conditions.[3] NMP proceeds via homolytic dissociation of a terminal alkoxyamine group and therefore all chains behave directly as radical initiators. Due to its simplicity (i.e., use of a single molecule to serve as both the initiator and the control agent), it was the first one to be successful in complex polymerization systems such as aqueous miniemulsion, dispersion, and emulsion polymerizations,[4−7] the latter being the most important technique in aqueous dispersed systems from the industrial viewpoint. The best conditions for success in emulsion polymerization were met with the development of water-soluble alkoxyamine initiators. The BlocBuilder alkoxyamine based on the nitroxide SG1 (Scheme 1) was used in a two-step process in the presence of surfactant.[7,8] A step forward was achieved when water-soluble macromolecular alkoxyamines were used in batch, ab initio, surfactant-free emulsion polymerization processes.[9−12] These polymerization systems operate via in situ chain extension of the hydrophilic living precursor by addition of hydrophobic monomers, and concomitant self-assembly of the so-formed amphiphilic block copolymer chains, following the so-called polymerization-induced micellization mechanism. Spherical micelles were observed in most examples.[9−12] Other morphologies were also found (elongated micelles and vesicles) in very specific conditions, however, where the hydrophobic monomer was 4-vinylpyridine.[10] It then appeared to us that NMP in aqueous emulsion[8−12] could be a very efficient and simple means to create, in one step, the traditional nano-objects that are usually obtained via block copolymer self-assembly using multistep techniques.[13−19] The method would have all the advantages associated with the conventional emulsion polymerization process and would lead to concentrated aqueous suspensions, obtained in the absence of both organic cosolvent and particular emulsification techniques. The formation of a single and predetermined morphology under these simple synthetic conditions is particularly appealing but requires the clean and homogeneous growth of the hydrophobic block throughout the process. Our work in the domain

Scheme 1. Synthetic Principle of NMP Carried Out in Emulsion Using the Macroalkoxyamine P(MAA$_{41}$-co-SS$_{10}$)-SG1 as an Initiator
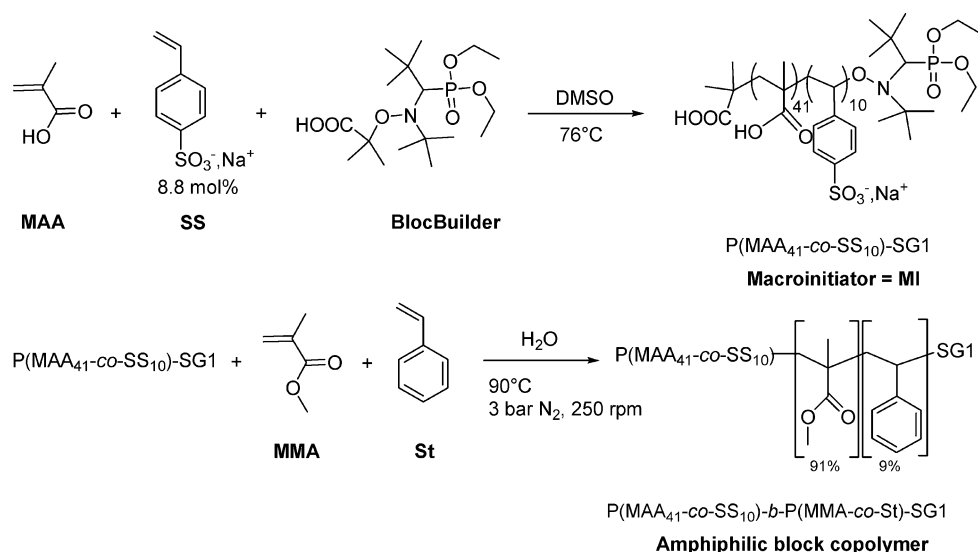
Table 1. Experimental Conditions for the Surfactant-Free, Ab Initio, Batch Emulsion Polymerization of MMA with 9.0 mol % of St at 90 °C[a]

expt	[MMA]$_0$ (mol·L$^{-1}_{aq}$)	[St]$_0$ (mol·L$^{-1}_{aq}$)	[NaOH]$_0$ (mol·L$^{-1}_{aq}$)	[MI]$_0$ (mmol·L$^{-1}_{aq}$)	target M_n[b] (g·mol^{-1})
1	2.26	0.24	0.67	13.8	23790
2	2.25	0.23	0.36	7.6	38260
3	2.26	0.24	0.36	7.6	38770
4	2.24	0.23	0.20	3.9	68390

[a]Initiated by the P(MAA$_{41}$-co-SS$_{10}$)-SG1 macroinitiator (MI) and a reaction time of 180 min pH = 7. [b]Theoretical number-average molar mass at 100% conv., calculated according to $M_n = M_n$ (MI) + conversion × weight of monomers (MMA + St)/initial mol number of MI.

was essentially carried out using the reversible addition–fragmentation chain transfer (RAFT)[20] CRP method, with poly((meth)acrylic acid-co-poly(ethylene oxide) methyl ether (meth)acrylate) trithiocarbonate macromolecular RAFT agents.[21−23] While we were interested in emulsion polymerization exclusively, other groups applied RAFT to nonaqueous and aqueous dispersion polymerization to also target non-spherical nano-objects.[24−27] It is, however, difficult to achieve for the moment 100% of a given morphology in emulsion polymerization, possibly due to the constant supply of radicals that is required to keep the controlled feature of RAFT. In this respect, NMP seems to be particularly appropriate.

This work is thus dedicated to the development of surfactant-free, ab initio, batch NMP in emulsion using a water-soluble alkoxyamine macroinitiator (MI) with the aim of producing well-defined morphologies through simultaneous formation and self-assembly of amphiphilic block copolymers in water.

The selected system is based on methacrylate main monomers (methacrylic acid, MAA, for the hydrophilic segment and methyl methacrylate, MMA, for the hydrophobic one), both copolymerized with a low percentage of a styrenic monomer (sodium 4-styrene sulfonate, SS, and styrene, St, respectively) to turn the nonliving NMP of methacrylate monomers into a living NMP performed at low temperature (Scheme 1).[28−30]

The copolymer of MAA with 8.8 mol % of SS was synthesized in DMSO solution at 76 °C using the BlocBuilder alkoxyamine initiator, following an already published protocol.[12] The structure of the copolymer purified by precipitation in dichloromethane was P(MAA$_{41}$-co-SS$_{10}$)-SG1 (with indica-

tion of the average number of subunits in the copolymer chains), as determined from size exclusion chromatography analysis (SEC of the copolymers performed after methylation of the carboxylic acid groups[31] in DMF + LiBr, 0.01 mol·L^{-1}, at 70 °C at a flow rate of 1.0 mL.min^{-1}; number-average molar mass: M_n = 5600 g·mol^{-1}; polydispersity index: M_w/M_n = 1.4, determined using a differential refractive index detector and PMMA calibration) and from ^{1}H NMR analysis of the average composition.

The emulsion polymerizations of MMA with 9.0 mol % of St were carried out at 90 °C in the presence of NaOH (pH ~ 7) and different concentrations of MI so as to target different molar masses for the hydrophobic segment. The experimental conditions are given in Table 1 and in the Supporting Information.

The system was based on batch conditions with all reactants introduced initially in the reactor in the absence of surfactant or radical initiator. As MMA and St are slightly soluble in water (saturation concentration: 6 × 10^{-3} mol·L^{-1} for St at 70 °C and 0.15 mol·L^{-1} for MMA at 80 °C), the polymerization starts in the aqueous solution upon homolytic dissociation of the alkoxyamine end-group. This leads to chain extension and the formation of a hydrophobic block attached to the hydrophilic macroinitiator segment. When the hydrophobic block reaches a critical length, self-association of the so-formed amphiphilic block copolymers induces nucleation. At this stage, the hydrophobic core of the nanoobjects swells with monomer and becomes the main polymerization locus. The conversion versus time and M_n versus conversion plots (Figure 1a,b) indeed support this mechanism, showing that polymerizations
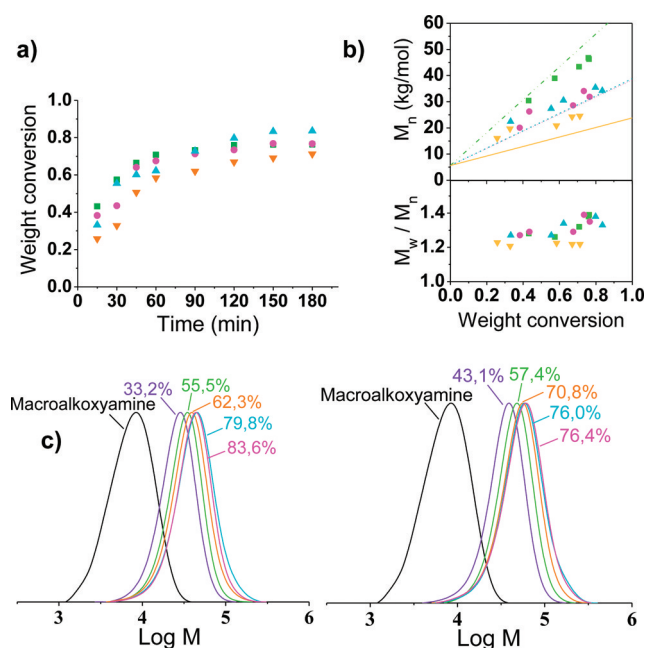
Figure 1. Kinetic characteristics of the emulsion copolymerizations of MMA and St at 90 °C, initiated by the P(MAA$_{41}$-co-SS$_{10}$)-SG1 macroalkoxyamine. (a) Evolution of the weight conversion vs time; (b) Evolution of number-average molar masses (M_n) and polydispersity index (M_w/M_n) vs conversion (the straight lines correspond to the theoretical evolution): expt. 1, orange ▼; expt. 2, pink ●; expt. 3, blue ▲, expt. 4, green ■ (see Table 1); (c) SEC peaks as a function of the overall conversion for the expt. 3 (left) and expt. 4 (right).

Figure 2. Aspect of the final polymer aqueous dispersions, as a function of the P(MAA$_{41}$-co-SS$_{10}$)-SG1 macroinitiator concentration, that is, the final target chain length.

concentration, expt. 1), the final medium was a translucent suspension indicating the presence of very small objects (intensity average diameter = 39 nm, as measured by dynamic light scattering (DLS), with a dispersity factor of 0.1). When the macroinitiator concentration was decreased, that is, the hydrophobic block molar masses at final conversion became larger, the systems was hazier and particularly viscous for the expt. 3.

The samples were further analyzed by transmission electron microscopy (TEM) (Figure 3), which confirmed the aspect of the suspensions by showing the size and shape of the formed nano-objects. For the shortest hydrophobic block, only spheres of very small diameter were formed (number average diameter = 25 nm; expt. 1), in agreement with the DLS analysis and with the translucent aspect of the suspension. When the molar mass of the hydrophobic block was increased, a mixture of spheres (diameter = 18 nm) and elongated micelles (diameter: 42 nm; expt. 2) first and then only very long and homogeneous nanofibers (expt. 3, length > 2 μm, diameter = 30−40 nm) were observed (Figure 3). Their presence explained the white and very viscous state of the dispersion. In this expt. 3, spheres and elongated micelles formed first and then turned into 100% fibers within 1 h of polymerization (i.e., 60% conversion; see the TEM images in the Supporting Information). Finally, with a further increase of the hydrophobic segment molar mass, vesicle-like nano-objects were formed, that were homogeneous in shape but rather heterogeneous in size however (diameter ranging from 90 to 700 nm approximately).

For a given molar mass of the hydrophilic component, the correspondence between the molar mass of the hydrophobic block and the final particle morphology corresponded to classical observations made for amphiphilic block copolymer self-assemblies achieved via different processes.[16] This result indicates that geometric and thermodynamic factors also play a role here in the implied mechanism, along with polymerization kinetic factors.

The rheological properties of the final dispersion of expt. 3 were further analyzed without dilution (i.e., concentration of 16 wt %). The results showing the storage modulus (G') and the viscous modulus (G'') as a function of frequency are shown in Figure 4. It appeared very clearly that the dispersion behaved as a viscoelastic solid with G' being one order of magnitude larger than G'' over the whole frequency range explored, in agreement with the presence of entangled objects.

In conclusion, NMP using water-soluble macroalkoxyamine initiator is a particularly well-suited method for polymerization-induced micellization. As it leads to a very clean control over molar masses, the amphiphilic block copolymers formed in situ self-assemble according to the length of the hydrophobic blocks into nanoobject with well-defined morphologies. The most intriguing and spectacular one is the nanofiber type of organization. They are nonaggregated self-stabilized structures

occurred until high conversion and proceeded via chain extension of the MI. It was corroborated by the consumption of the MI as shown by the complete shift of the SEC peaks (Figure 1c). The polymerizations met all the criteria of a living system as the experimental values of M_n increased linearly with monomer conversion and the SEC peaks continuously shifted toward higher molar mass values, without any tailing, indicative of a narrow molar mass distribution (low polydispersity indexes). From these results (also summarized in Table 2) it

Table 2. Monomer Conversions, Macromolecular Characteristics of the Final Amphiphilic Block Copolymers and Properties of the Aqueous Dispersions

expt.	conv. (%)	solids content (%)	$M_{n,SEC}$[a] (kg·mol^{-1})	M_w/M_n	nano-object morphologies
1	71	13.2	24.6	1.22	spheres
2	77	14.6	31.9	1.35	spheres + short fibers
3	84	16.0	34.2	1.33	fibers
4	76	14.7	46.3	1.39	vesicles

[a]Experimental number-average molar mass obtained with SEC in DMF with 0.01 mol·L^{-1} LiBr using PMMA calibration (carboxylic acids were methylated[31] for the analysis and the molar mass of the ester groups was further subtracted).

is, thus, clear that our polymerizations obeyed the principles of NMP based on an activation−deactivation equilibrium between the propagating macroradicals and the dormant chains.

All polymerizations led to stable aqueous polymer suspensions, the aspect of which was strongly dependent on the initial macroinitiator concentration (Figure 2). When low molar mass hydrophobic block was targeted (i.e., high MI
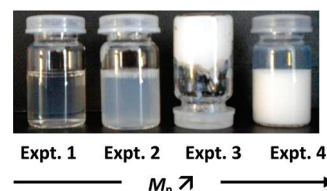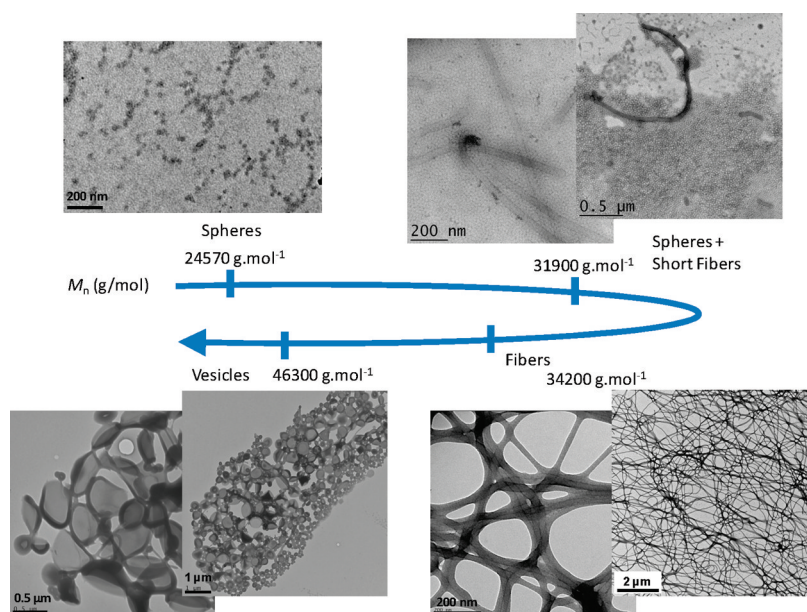
Figure 3. TEM images of the final nanoobjects obtained from different hydrophobic block molar masses for a same macroinitiator P(MAA$_{41}$-*co*-SS$_{10}$)-SG1 (5600 g·mol^{-1}).
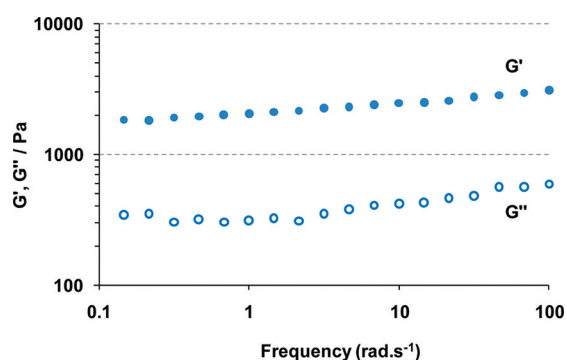

Figure 4. Rheological behavior of the final aqueous dispersion of expt 3: elastic modulus (G') and viscous modulus (G'') as a function of frequency measured at a strain of 0.5%.

with very large aspect ratio obtained directly in water dispersions. They exhibit a hydrophilic polymer shell that can be easily postfunctionalized through the carboxylic acid groups. These objects might be used in a variety of applications in materials science.

ASSOCIATED CONTENT

Supporting Information

Full experimental data outlining synthesis and analytical techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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