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# 1,4-Polybutadiene-Based Particles Prepared by Aqueous Suspension Ring-Opening Metathesis Polymerization

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ABSTRACT: This paper describes two different strategies to obtain stable beads of 1,4-polybutadiene (PB) by suspension ring-opening metathesis of 1,5-cyclooctadiene carried out in water. Both rest on the use of amphiphilic stabilizing agents whose hydrophilic/hydrophobic balance was finely tuned. A norbornenyl-ended poly(styrene-*b*-ethylene oxide) macromonomer and an in situ prepared poly(butadiene-*g*-ethylene oxide) graft copolymer provided the required stability for PB beads in the range of 20 $\mu$m to remain suspended in water.

## Introduction

Producing pure 1,4-polybutadiene (PB) in the particle form via aqueous polymerizations still remains an important challenge. Only transition-metal polymerizations provide a precise control of the microstructure of the polybutadiene chains formed, but their intolerance of protic and polar functions has precluded the use of water in their presence. Consequently, industrially prepared stereoregular rubbery materials are obtained by solution polymerizations in organic and apolar media. However, a great deal of effort has been made to develop water-tolerant initiators that could be used in aqueous heterogeneous processes. Compared to solution polymerizations, the latter offer several technical advantages, such as a higher rate of reaction or a better control of the polymerization process, etc.

As early as 1965, Rinehart et al.[1] prepared *trans*-1,4-PB by coordinative emulsion polymerization using rhodium- and ruthenium-based metal salts as catalysts. Low yields and various practical problems have deterred the large scale implementation of these aqueous polymerizations. More recently, Henderson et al.[2] described a process of polymerization of butadiene in water. Microcapsules of polyene were first synthesized and used to microencapsulate the catalyst components (cobalt, alkylaluminum, and carbon disulfide) so as to subsequently protect them from water. Such a microencapsulated catalyst then served to promote the suspension polymerization of butadiene in water, yielding syndiotactic 1,2-PB particles. In a recent addition, Ono et al.[3] also contributed to the subject by using a similar cobalt catalyst to initiate the emulsion polymerization of butadiene in water.

In recent years, ring-opening metathesis polymerization (ROMP) has gained widespread interest as a versatile method to synthesize various polyalkenamers. When applied to 1,5-cyclooctadiene (COD), ROMP affords an exclusively linear PB with a 1,4-type microstructure.[4] Within the past 10 years, the development of a new generation of initiators based on late transition metals has expanded its use to a variety of conditions including polar and protic media.[5] By using ruthenium-based initiators such as $(PCy_3)_2Cl_2Ru{=}CHPh$,[6] we succeeded in the preparation of 1,4-PB particles in a dichloromethane/ethanol medium via dispersion ROMP.[7−9] Under proper conditions, such a ruthenium alkylidene was successfully applied to initiate the polymerization of COD in water. Claverie et al. indeed obtained a polybutadiene latex under miniemulsion conditions.[10]

In this study, a new method of polymerization of COD by suspension ROMP carried out in water was contemplated using $(PCy_3)_2Cl_2Ru{=}CHPh$ as catalyst. In such a process, the monomer was dispersed as droplets in an aqueous phase under vigorous agitation. A suspending agent was added to prevent coalescence of particles during the reaction. Because of the initiator solubility in the monomer phase, the polymerization occurred within the monomer droplets which gave rise to polymer beads as polymerization proceeded. In addition to a suspending agent, another type of stabilizer was found necessary to achieve a durable and effective colloidal stability. Various strategies of costabilization were thus contemplated: in particular, poly(ethylene oxide) (PEO) macromonomers were copolymerized with COD so as to generate in situ stabilizing species for the PB beads. PB-*g*-PEO graft copolymers separately prepared have also been used to help the stabilization of the PB beads. The results of these experiments are thoroughly discussed and commented on in regard to the colloidal stability of the particles formed.

## Experimental Section

**Materials.** 1,5-Cyclooctadiene was kept over $CaH_2$ and then freeze vacuum distilled. ROMP reactions were carried out under steady flow of purified nitrogen using distilled and deionized water. The ruthenium-based complex $(PCy_3)_2Cl_2Ru{=}CHPh$ was prepared by following the literature method.[11] α-Norbornenyl poly(ethylene oxide) macromonomers based on poly(ethylene oxide) (**1**, **2**, **3**, Scheme 1) have been prepared according to the procedure described in the literature.[12,13] The latter were dried and stored under an inert atmosphere. Poly(diallylmethylammonium chloride), with an average molar mass ranging from 200 000 to 350 000 g/mol, was used as suspending agent.

**Methods.** Conversion of 1,5-cyclooctadiene was determined by gas chromatography with a trace of undecane as internal standard. Conversion of macromonomer was monitored by size exclusion chromatography (SEC) using poly(ethylene oxide) as internal standard ($\bar{M}_n$ = 1500 g mol$^{-1}$). The SEC equipment

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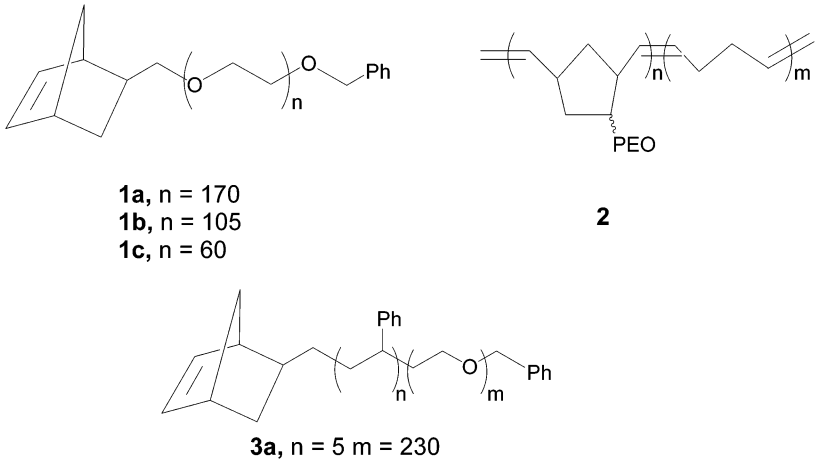
**Scheme 1. Poly(ethylene oxide) Additives Used as Stabilizers**



**1a,** n = 170
**1b,** n = 105
**1c,** n = 60

**2**

**3a,** n = 5 m = 230
**3b,** n = 23 m = 170

**Table 1. Characteristics of 1,4-Polybutadiene Particles Stabilized by a Suspending Agent (A) or by the Steric Action of a Suspending Agent and That of a PEO Macromonomer (1a) (B, C, D, E)**

| experiment | A | B | C | D | E |
|---|---|---|---|---|---|
| NB−PEO (**1a**), g | | 0.7 | 0.7 | 0.7 | 0.7 |
| $\bar{M}_n$(NB−PEO), g/mol | | 7500 | 7500 | 7500 | 7500 |
| COD, mL | 4 | 4 | 4 | 4 | 4 |
| water, mL | 80 | 80 | 80 | 80 | 80 |
| I, mg | 15 | 15 | 15 | 15 | 15 |
| suspending agent, mL | 4 | 4 | 4 | 4 | 4 |
| agitation rate, rpm | 600 | 600 | 600 | 600 | 600 |
| temperature, °C | 25 | 25 | 25 | 50 | 70 |
| procedure | procedure I (see experimental part) | procedure II + (**1** dissolved in the continuous medium) | procedure II | procedure II | procedure II |
| system stability | slow coagulation | slow coagulation | slow coagulation | slow coagulation | slow coagulation |
| Dn(LALLS), $\mu$m | 0.2−1.5 mm | 0.2−1.5 mm | 0.2−1.5 mm | 0.2−1.5 mm | 0.2−1.5 mm |
| Dn(OM), $\mu$m | 10−400 $\mu$m polydisperse | 10−400 $\mu$m polydisperse | 10−400 $\mu$m polydisperse | 10−400 $\mu$m polydisperse | 10−400 $\mu$m polydisperse |
| COD conversion, wt % | 100 | 100 | 100 | 100 | 100 |
| PEO content of particles, wt % | - | 6 | 9 | 9 | 10 |

consists of a JASCO HPLC pump type 880-PU, TOSOHAAS TSK gel columns, a Varian refractive index detector, and a JASCO 875 UV/vis absorption detector, THF being the mobile phase. NMR spectra were obtained using a Bruker AC 200 spectrometer. The particle sizes were determined by static light scattering (SLS), optical microscopy (OM), and scanning electron microscopy (SEM). The presence of micellar aggregates was detected by dynamic light scattering (DLS) analysis. DLS measurements were performed using a MALVERN zetasizer 3000 equipped with a He−Ne laser. Before measurements, latexes were diluted about 100 times to minimize multiple scattering caused by high concentration. A MASTERSIZER instrument was used to analyze submicrometric particles by laser diffraction based on low-angle laser light scattering (LALLS) techniques. SEM pictures were performed with a JEOL JEM-2010 scanning electron microscope. Particle sizes were also measured by optical microscopy (OM) using a Sony Laborlux microscope.

**Procedure I. Preparation of 1,4-Polybutadiene Particles by Suspension ROMP of 1,5-Cyclooctadiene (Entry A, Table 1).** Suspension polymerization was carried out in a 250 mL glass reactor equipped with a triple blade propeller stirrer. Vertical baffles were installed near the walls of the reactor so as to obtain homogeneous mixing. 80 mL of water containing 1% poly(diallylmethylammonium chloride) solution was first introduced into the reactor, stirred at 600 rpm, and flushed with nitrogen for 60 min. A shot of COD ($3.3 \times 10^{-2}$ mol) was then introduced to the reactor under nitrogen. After 7 min of mixing, the Grubbs catalyst ($1.8 \times 10^{-5}$ mol) dissolved in a small volume of dichloromethane (0.5 mL) was added to the reactor in order to initiate the polymerization. The reaction was shown to be complete after ~2 h when spherical polybutadiene beads were formed.

**Procedure II. Suspension ROMP of 1,5-Cyclooctadiene in the Presence of a PEO (1) or PS−PEO (3) Macromonomer as Stabilizer (Entries B, C, D, E, N, O, Tables 1 and 3).** A similar procedure was conducted except that a macromonomer charge ($9.3 \times 10^{-5}$ mol) was either previously dissolved in water before the beginning of the polymerization (entry B, Table 1) or mixed with COD and 1 mL of $CH_2Cl_2$ to form an organic solution (entries C, D, E, Table 1 and N, O, Table 3). The latter was then added to the suspension reactor under nitrogen. The reaction was carried out at this temperature for 2 h.

**Procedure III. Suspension ROMP of 1,5-Cyclooctadiene in the Presence of a Preformed PB-*g*-PEO Graft Copolymer as Stabilizer (Entries F, G, H, I, J, K, L, M, Table 2).** Suspension copolymerization was conducted in a similar 250 mL glass reactor at 70 °C. Water (80 mL) containing 1% poly(diallylmethylammonium chloride) solution was first introduced into the reactor, stirred at 600 rpm, and flushed with nitrogen for 60 min. Then COD ($3.3 \times 10^{-2}$ mol) preliminary mixed with NB−PEO macromonomer ($9.3 \times 10^{-5}$ mol) of $\bar{M}_n = 7500$ g/mol and 1 mL of $CH_2Cl_2$ were added. The initiator ($1.8 \times 10^{-5}$ mol) dissolved in 0.5 mL of $CH_2Cl_2$ was then added in this homogeneous solution, and the resulting reactive phase (COD, NB−PEO, Grubbs catalyst, $CH_2Cl_2$) was introduced in one shot into the reactor. The reaction was carried out at this temperature for 2 h.

## Results and Discussion

**I. First Approach toward the Colloidal Stability of the Polybutadiene Particles.** In a typical process (procedure I, see experimental part), the monomer (COD) was dispersed in a form of liquid droplets in

**Table 2. Characteristics of 1,4-Polybutadiene Suspension Stabilized by the Combined Effect of a Suspending Agent and a PB-*g*-PEO Graft Copolymer (See Experimental Part, Procedure III)**

| experiment | F | G | H | I | J | K | L | M |
|---|---|---|---|---|---|---|---|---|
| stabilizer, g | 0.7<br>NB−PEO<br>**1a** | 0.7<br>NB−PEO<br>**1a** | 0.7<br>NB−PEO<br>**1a** | 0.7<br>NB−PEO<br>**1a** | 0.7<br>NB−PEO<br>**1a** | 0.7<br>NB−PEO<br>**1a** | 0.7<br>NB−PEO<br>**1a** | 0.7<br>NB−PS−PEO<br>**1b** |
| $\bar{M}_n$(stabilizer), g/mol | 7500 | 4700 | 2700 | 7500 | 7500 | 7500 | 7500 | 9900 |
| COD, mL | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| water, mL | 80 | 80 | 80 | 80 | 80 | 80 | 80 | 80 |
| I, mg | 15 | 15 | 15 | 15 | 30 | 15 | 15 | 15 |
| suspending agent, mL | 4 | 4 | 4 | 0 | 4 | 4 | 4 | 4 |
| agitation rate, rpm | 600 | 600 | 600 | 600 | 600 | 600 | 600 | 600 |
| temperature, °C | 70 | 70 | 70 | 70 | 70 | 50 | 25 | 70 |
| COD droplets | fine (turbid) | fine (turbid) | large (no turbidity) | fine (turbid) | fine (turbid) | fine (turbid) | fine (turbid) | fine (very turbid) |
| system stability[a] | o | * | *** | ** | * | ** | *** | o |
| Dn(LALLS)[b] | 10 μm | 4.6 μm | 0.2−1.5 mm |  | 7 μm | 44 μm | 0.2−1.5 mm | bimodal:139 nm (165 nm[c]) and 11 μm |
| Dn(OM), μm | 5−35 | 2−50 | 10−400 |  | 5−50 | 48 | 10−400 | <20 |
| COD conversion, wt % | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 30 |
| PEO content of particles,[d] wt % | 46 | 55 | 7 |  | 63 | 20 | 12 | 100 |

[a] o = stable, no sign of aggregation. * = traces of aggregation are observed. ** = many aggregation areas are observed; a stable dispersed phase has been separated and characterized, however. *** = coagulation; a shapeless polymer bulk is rapidly obtained. [b] Determined by low-angle laser light scattering (LALLS). [c] Determined by quasi-elastic light scattering (QELS). [d] Determined by the ratio $100m_p(\mathrm{Macr})/m_0(\mathrm{Macr})$ with $m_p(\mathrm{Macr})$ = weight of macromonomer incorporated in the centrifuged particles, $m_0(\mathrm{Macr})$ = weight of macromonomer introduced. $m_p(\mathrm{Macr})$ was determined by resolving the following equation: $\{m_p(\mathrm{COD})/\bar{M}(\mathrm{COD}) \times 4\}/\{m_p(\mathrm{Macr})/[\bar{M}_n(\mathrm{Macr})N(\mathrm{OE}) \times 4]\} = I_2/I_1$, with $I_1$ = intensity of the oxirane protons of PEO ($\delta(\mathrm{CH_2O}) = 3.6$ ppm), $I_2$ = intensity of the ethylenic protons of polybutadiene ($\delta(\mathrm{C{=}C{-}H}) = 5.27{-}5.34$ ppm), $m_p(\mathrm{COD})$ = weight of polybutadiene incorporated in the centrifuged particles (integral of COD consumed is supposed to be incorporated inside particles), $\bar{M}(\mathrm{COD})$ = molar mass of COD = 108 g/mol, $\bar{M}_n(\mathrm{Macr})$ = molar mass of macromonomer, and $N(\mathrm{OE})$ = number of oxyethylene units on a macromonomer chain.

**Table 3. Characteristics of 1,4-Polybutadiene Suspension Stabilized by a Suspending Agent and a NB−PS−PEO Macromonomer (3a, 3b) (See Experimental Part, Procedure II)**

| experiment | N | O |
|---|---|---|
| NB−PS-*b*-PEO | **3a** | **3b** |
| NB−PS-*b*-PEO, g | 0.7 | 0.7 |
| $\bar{M}_n$(NB−PS−PEO), g/mol | 10700 (no surfactant properties) | 9900 (surfactant properties) |
| $\bar{M}_n$(PEO), g/mol | 10100 | 6800 |
| $\bar{M}_n$(PS), g/mol | 500 | 2400 |
| COD, mL | 4 | 4 |
| water, mL | 80 | 80 |
| I, mg | 15 | 15 |
| suspending agent, mL | 4 | 4 |
| agitation rate, rpm | 600 | 600 |
| temperature, °C | 70 | 70 |
| procedure | procedure II (experimental part) | procedure II |
| system stability | stable | stable |
| Dn(LALLS), μm | 19 | several populations 100 nm−200 μm |
| Dn(OM), μm | 19.2 | 2−150 polydisperse |
| conversion COD, wt % | 100 | 42 |
| conversion macromonomer, wt % | 100 | 100 |

water. Vigorous stirring (600 rpm) was applied and a suspending agent added. The polymerization was then initiated at ambient temperature by addition of an organic solution containing the catalyst. After 2 h of reaction, jelly-like PB beads in the hundred micrometer size range could be generated, but the latter appeared poorly stabilized (entry A, Table 1). Discontinuation agitation caused indeed a slow aggregation. Because of the very low glass transition temperature exhibited by 1,4-polybutadiene ($T_g = -106$ °C for *cis*-1,4 and −107 °C for *trans*-1,4), the beads began adhering to each other as illustrated by the microscope pictures (Figure 1). Unfortunately, no improvement could be obtained upon increasing the rate of stirring, varying the nature of the suspending agent, its concentration, and the temperature of reaction, etc. Nonetheless, a complete conversion in COD was observed, suggesting that $(\mathrm{PCy_3})_2\mathrm{Cl_2Ru{=}CHPh}$ ruthenium−alkylidene is tolerant of water. Given the well-known difficulties encountered for polymerizing this cycloolefin of low ring strain energy,[9,10] this result must also be considered as a remarkable feature.

**I.1. Poly(ethylene oxide) Macromonomer as Reactive Stabilizer.** To prevent the beads from flocculating, the opportunity of using a poly(ethylene oxide) macromonomer fitted with a norbornenyl reactive unsaturation (**1**) was considered. Actually, very few studies reported the use of a macromonomer as a stabilizer within a suspension process.[14,15] The copolymerization of **1** with 1,5-cyclooctadiene resulted in the formation of 1,4-polybutadiene-*g*-poly(ethylene oxide) graft copolymers (PB-*g*-PEO) with expectedly interesting stabilizing properties (Scheme 2).

In a previous contribution, PEO macromonomers were shown to efficiently stabilize the dispersion polymerization of COD[7−9] or norbornene.[7,16] Unlike the case of dispersion, a suspension process is a bulk polymerization that occurs from the very beginning in a heterogeneous medium within the monomer droplets. Given its nature, the NB−PEO macromonomer added to the medium has thus the opportunity to partition between two different phases: the continuous medium (water) and the monomer droplets. At first sight, such PEO macromonomers seem not appropriate for a copolymerization with COD under the conditions of suspension polymerization. Indeed, the NB−PEO carries a very short hydrophobic reactive entity (NB) and a rather long PEO chain water-soluble ($\bar{M}_n$ = 7500 g/mol).

Nonetheless, a first attempt at copolymerizing **1** (entry B, Table 1) after its dissolution in water resulted in a modest 6% incorporation as expected and a slow flocculation. Obviously, such a small extent of incorpo-

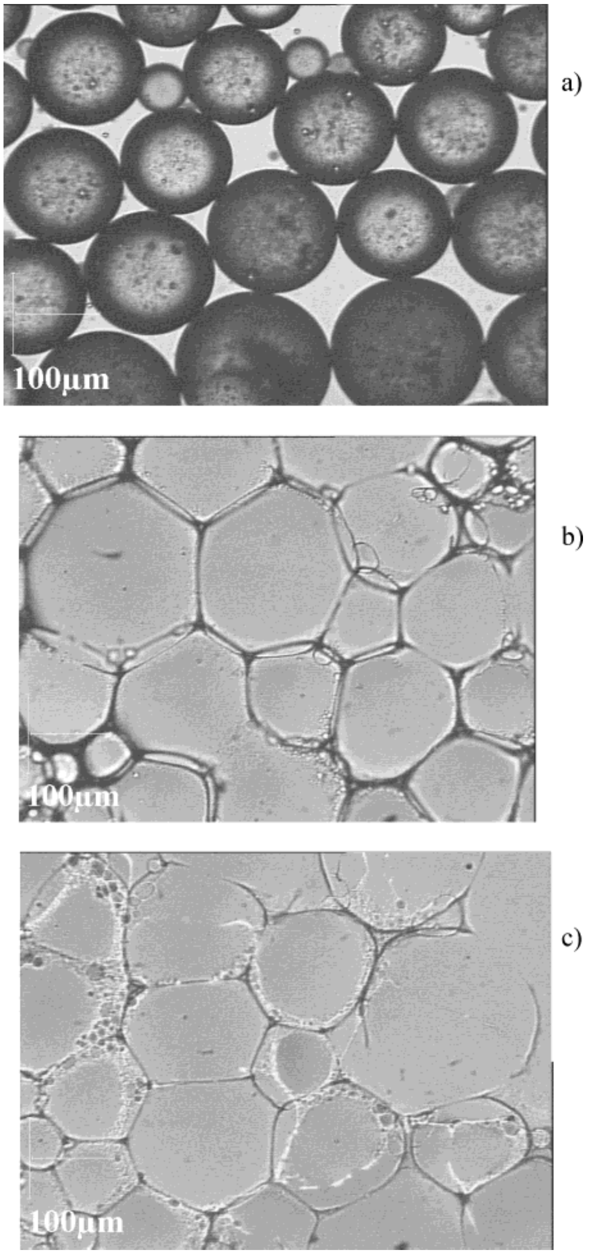


**Figure 1.** OM pictures of PB particles synthesized by suspension ROMP of COD without costabilizer: (a) immediately, (b) 10 min, and (c) 30 min after the end of agitation.

ration was not enough to stabilize the beads. The rest of NB−PEO remained unreacted in water or formed water-soluble PEO-rich graft copolymers. Again, polymerization of COD went to completion. Unfortunately, the strong hydrophilic character of PEO macromonomers prevented them from diffusing to the droplets' surface and copolymerizing with COD.

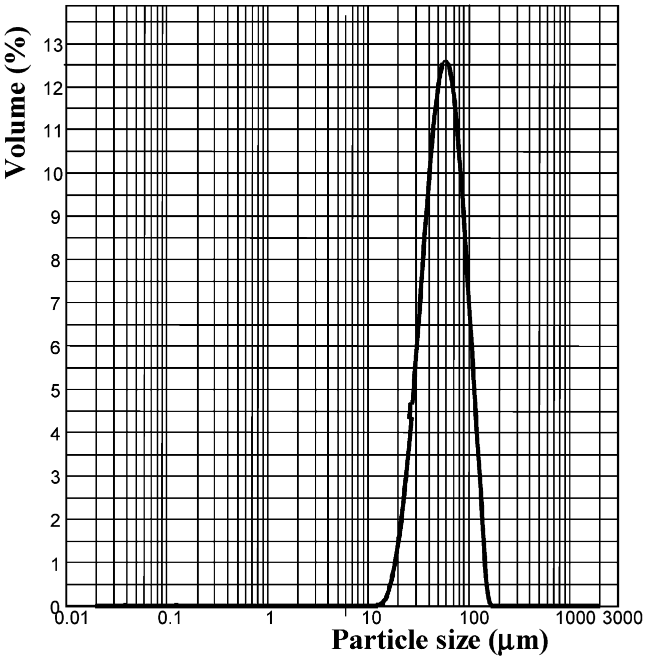


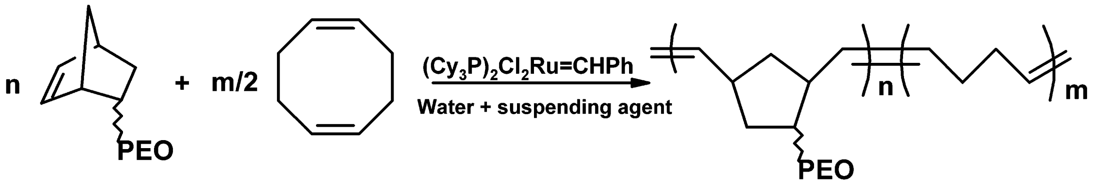
**Figure 2.** LALLS analysis of the COD droplets formed in the presence of **1**.

**Effect of the Method of Addition of 1.** To overcome this problem, **1** was predissolved in COD with a small amount of organic solvent, and then the resulting solution was added to the continuous medium (entry C, Table 1). The droplets' sizes were investigated by LALLS: smaller droplets were measured (Dn = 57 $\mu$m) compared to the size range found for those formed in absence of **1** (Dn = 150 $\mu$m) (Figure 2). The introduction of a catalyst solution triggered the polymerization. Again, the suspension quickly coalesced after 1 h of reaction without any significant increase of the PEO content in the polymer product formed (9%). This result again evidenced that macromonomer chains initially present at the surface of the COD droplets eventually migrate to the aqueous phase where most of them remain unreacted.

**Effect of Reaction Temperature.** Another strategy aiming at the decrease of the macromonomer water solubility by increase of the temperature was considered to minimize its waste during polymerization.[19] Upon increase of the temperature, affinity of **1** for the monomer droplets should therefore be enhanced, which would normally favor the conversion of **1** and thus a better colloidal stability. Unfortunately, the temperature was raised successively to 50 °C (entry D, Table 1) and 70 °C (entry E, Table 1) without preventing the formation of a precipitate.

**I.2. Conclusion about the Use of PEO Macromonomer as Reactive Stabilizer.** Our first attempts to copolymerize **1** with COD under suspension conditions thus failed to provide stable polymer beads, mainly because of the too hydrophilic character of **1**. Two alternatives were contemplated to prevent the

**Scheme 2. Suspension ROMP Reaction of 1,5-Cyclooctadiene (COD) in Water and in the Presence of a α-Norbornenyl Poly(ethylene oxide) Macromonomer (NB−PEO, 1)**



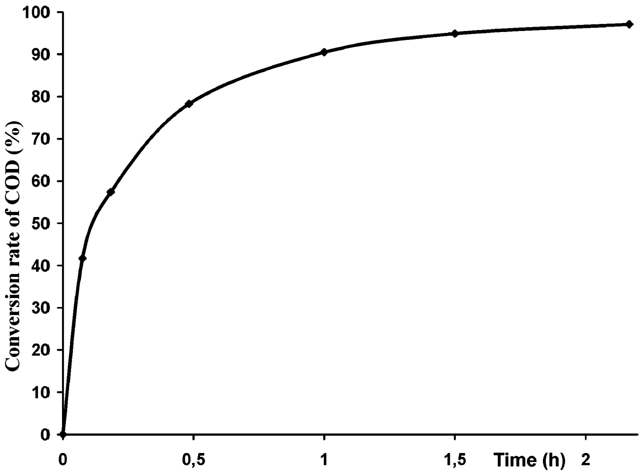


**Figure 3.** Conversion of 1,5-cyclooctadiene vs time for aqueous suspension ROMP in the presence of **2** as stabilizer.

stabilizer from migration to the continuous medium: amphiphilic structures that contain a hydrophobic part in addition to the PEO moiety such as PB-*g*-PEO graft copolymers **(2)** and NB−PS−PEO macromonomers **(3)** were employed in the following polymerizations. The polybutadiene backbone in **2** and the polystyrene block in **3** should provide hydrophobicity necessary for the stabilizer to anchor at the particle/droplet surface.

**II. Suspension Polymerization of 1,5-Cyclooctadiene in the Presence of a PB-*g*-PEO Graft Copolymer (2) as Stabilizer.** We chose to prepare the PB-*g*-PEO-type stabilizer "in situ" through a reaction performed in solution (procedure III, see experimental part). To this end, (entry F, Table 2), an amount of initiator was added to an organic solution of monomer and macromonomer upon formation of PB-*g*-PEO graft copolymer (**2**) which occurs at once. The resulting solution was poured into a water-containing reactor where some suspending agent was added. The polymerization was then carried on under suspension conditions at 70 °C and with vigorous stirring. The site of propagation being now located within dispersed monomer droplets stabilized by the newly formed copolymer chains of **2**. After 2 h of reaction, a stable colloidal suspension could be eventually obtained with a very satisfactory yield (see Table 2).

**II.1. Kinetic Results: Initial Polymerization Step.** (i) Only 3% of COD was actually consumed during the first solution phase, demonstrating that most of monomer is polymerized within the reservoir droplets, as in a normal suspension process. (ii) As for NB−PEO, a higher proportion than COD—about 10%—converted during the solution polymerization because of the highly reactive norbornenyl entity.

This first step is thus a unique means to incorporate some macromonomer in the growing chains and to generate amphiphilic copolymers (PB-*g*-PEO) that can subsequently serve as stabilizers for monomer droplets and polymer particles. The marked turbidity resulting for the addition of **2** in the suspension reactor is well indicative of its good stabilizing properties.

**II.2. Kinetic Results: Suspension Polymerization Step.** (i) Figure 3 shows the conversion of COD with the polymerization time: 40% of COD was consumed after 5 min of reaction and 90% after 1 h. The slower rate of the second phase was attributed to the decreasing concentration of monomer in the polymer particles. A complete consumption was reported after 2 h of reaction. (ii) Contrary to COD, NB−PEO could not be polymerized to completion: its conversion reached a value of 46% after 5 min of reaction. This result shows that its copolymerization with COD occurred not only in solution but also in suspension. However, in the suspension reactor, a nonnegligible part of the macromonomer is certainly driven out of the monomer phase and transferred to the water continuous medium where it remains soluble. Nevertheless, the grafting of about half of the initial PEO macromonomer provided a sufficient protective barrier to stabilize the particles formed.

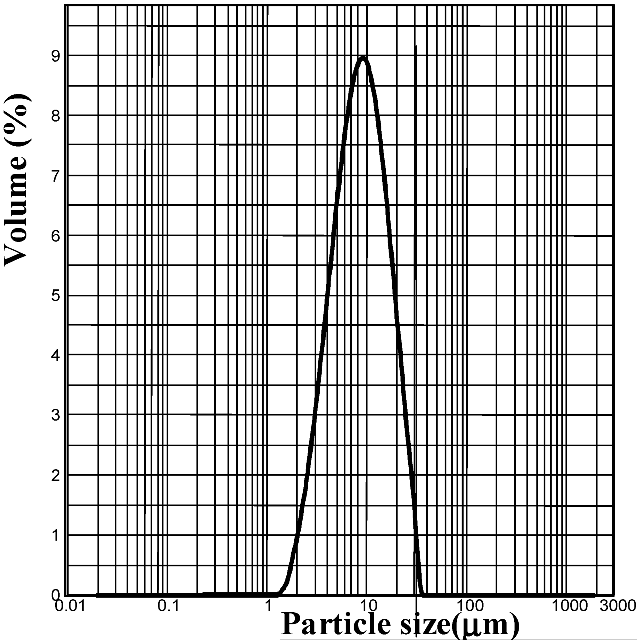


**Figure 4.** LALLS analysis of PB suspension in the presence of **2** (entry F, Table 2).

**II.3. Suspension Characterization.** The PB suspension was characterized by the use of various techniques: low-angle laser light scattering (LALLS), scanning electron microscopy (SEM), and optical microscopy (OM).

Figure 4, obtained by LALLS measurements, showed a monomodal but broadly distributed particle size ranging from 3 to 20 $\mu$m.

One can observe that the sizes found are particularly low compared to those usually obtained by free radical suspension polymerization, typically between 20 and 1000 $\mu$m. Such a difference is attributable to the stabilizing effects of PB-*g*-PEO graft copolymers that can be 2-fold:

First, they secure an efficient emulsification for monomer droplets (in combination with the suspending agent) by remaining at the oil−water interface and thus creating a steric barrier that prevents coalescence. Fine COD droplets can thus be produced, whose colloidal stability was evidenced by the absence of flocculation upon discontinuing agitation. Since particle size is known to heavily depend on that of initial monomer droplets, those that have a low average diameter should therefore give rise to small polymer particles.

Second, these PEO chains are covalently grafted onto the surface of particles unlike the adsorbed polymer chains of classical suspension polymerization. This could be also responsible for the improvement of colloidal

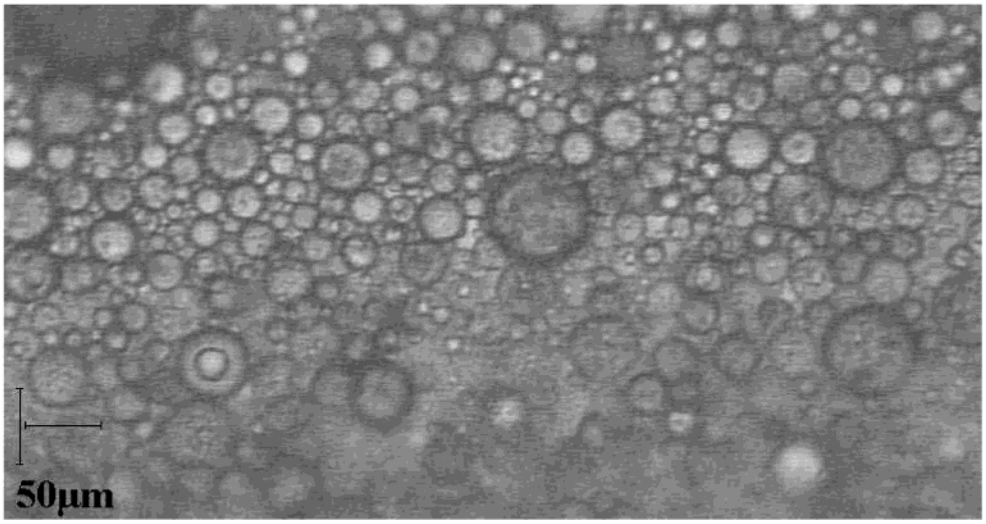


**Figure 5.** OM picture of PB particles synthesized by suspension ROMP of COD with **2** (entry F, Table 2).

stability and thus the generation of smaller size particles.

Figure 5 exhibits an OM picture of the polybutadiene-based particles, which appear spherical and well-stabilized. The latter were also found stable in water whether suspending agent was used or not. Despite the tendency of particles to aggregate when stripping of water (necessarily for the preparation of SEM samples), a smooth and regular particle surface was characterized by SEM (Figure 6). Because of thin-skimmed PEO layer at the surface of the soft polybutadiene core, it was possible to preserve the spherical shape of particles.

Finally, one can stress the good agreement between the data generated by LALLS, SEM, and OM regarding the particles' sizes (Table 2).

**II.4. Influence of Experimental Conditions on the Suspension Colloidal Properties.** Various experimental parameters were reviewed such as the macromonomer molar mass, the temperature, the initiator concentration, etc., and their impacts on the colloidal stability and the size of the particles formed examined.

**Effect of the Molar Mass of PEO Macromonomer.** Three PEO macromonomers (**1a**, **1b**, **1c**) of different molar mass were used: $\bar{M}_n = 7500$ g/mol (entry F, Table 2), $\bar{M}_n = 4700$ g/mol (entry G, Table 2), and $\bar{M}_n = 2700$ g/mol (entry H, Table 2). Macromonomers of a lower molar mass should exhibit a greater amphiphilic character due to the presence of the NB hydrophobic unsaturation. As a result, they should be polymerized to higher conversion thanks to their better affinity for the reactive monomer droplet. As expected, the limiting conversion reaches to 55% when using a macromonomer of 4700 g/mol (entry G, Table 2) as opposed to 46% with the one of larger molar mass (entry F, Table 2). Surprisingly, a poorer colloidal stability was found for experiment G, suggesting that the molar mass of the PEO chains has to be large enough for efficiently playing the role of stabilizer. After separation from aggregates, the stabilized particles were analyzed by SLS, which showed larger sizes.

The use of a macromonomer of 2700 g/mol molar mass (experiment H) surprisingly resulted in coagulation. Only 7% of macromonomer was actually incorporated into the polymer formed. The absence of turbidity upon addition of **2** in this case indicated a lack of stability. Large and colored monomer droplets were formed indeed after the addition of the preformed stabilizer whereas an instantaneous turbidity used to be observed in the presence of graft copolymers possessing branches of higher molar mass (entries F and G, Table 2). This can be considered as evidence that fine COD droplets were not formed and that the graft copolymer with its short PEO grafts is a poor stabilizer for the final polymer particles as well as the initial droplets.

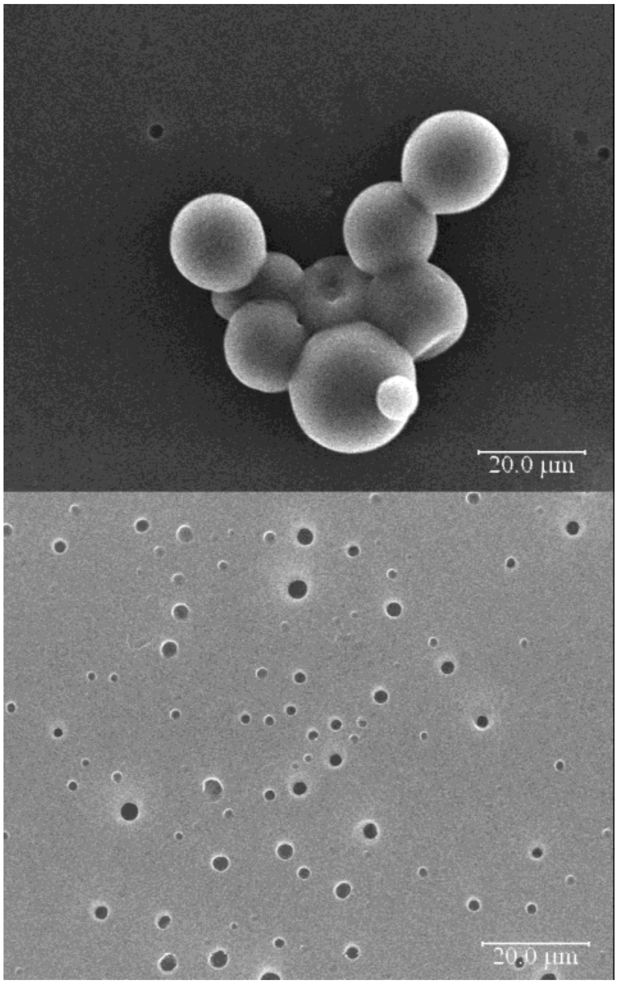


**Figure 6.** SEM pictures of PB particles synthesized by suspension ROMP of COD with **2** (entry F, Table 2).

**Effect of Suspending Agent Concentration.** The exact role played by the suspending agent in the stabilization of the particles formed was also examined. In addition to decreasing the interfacial tension between the monomer droplets and the aqueous phase, it also helps increasing the viscosity and creating a protective layer of adsorbed chains at the surface of particles. An experiment (entry I, Table 2) performed without suspending agent showed a serious lack of stability, providing the evidence that the colloidal stability is achieved not only through the grafting of PEO branches but also through the adsorption of the suspending agent.

**Effect of Initiator Concentration.** A higher initiator concentration should contribute to increase the amount of macromonomer consumed “and thus lower the proportion lost by migration”, thereby generating smaller particles. Upon increase of the initiator concentration (entry J, Table 2), slightly smaller particles were indeed produced even if some tendency to the coagulation as also observed. As expected, a higher conversion was also observed: 63% of **1a** was polymerized against 46% with 2 times less initiator concentration (entry F, Table 2).

**Effect of Reaction Temperature.** To investigate the effect of temperature, a set of experiments (entries K and L, Table 2) were performed using the same conditions as that of the experiment F, except that the polymerization temperature was decreased to 50 °C (entry K, Table 2) and 25 °C (entry L, Table 2). The conversion of **1a** should normally be lowered on account of the decrease of PEO solubility in COD and its parallel increase of solubility in water when decreasing temperature. As expected, clear signs of coalescence can be discerned with a lower temperature of reaction. This can well be ascribed to an insufficient amount of PEO being grafted on the particle surface. At 25 °C, only 12% of PEO macromonomer polymerized, leading to the particles’ aggregations. At 50 °C, a stable dispersed phase including 20% of **1a** could be produced but an important fraction of PB-rich products flocculated.

**Effect of the Nature of PEO Macromonomer.** The type of macromonomer was also investigated with a view of examining the influence of its amphiphilic character on the kinetics of polymerization as well as the colloidal characteristics of the particles formed.

A NB−PS−PEO macromonomer (**3b**) possessing a PEO block of same size as that of **1a** and an additional PS block ($\bar{M}_n = 2400$ g/mol) was polymerized (entry M, Table 2). Compared to its hydrophilic analogue (**1a**), the presence of a hydrophobic block in NB−PS−PEO should increase its affinity for the monomer droplets and thus favor higher conversions. One has to stress that such amphiphilic macromonomers can form micelles in water above their critical concentration. Preliminary quasi-elastic light scattering (QELS) measurements clearly proved that **2** self-assembles into micelles in the concentration range used. Such micelles may well disturb the suspension polymerization by acting as a second polymerization locus that can compete with the monomer droplets.

A stable suspension could however be obtained through the use of PB-*g*-(PS−PEO) graft copolymer as stabilizer. Surprisingly, NB−PS−PEO **3b** was consumed until completion whereas the conversion of **1a** never crossed 50%. Another surprising feature was the incomplete consumption of COD: this latter reached 50% of conversion after 2 h of reaction as opposed to 98% using **1a**.

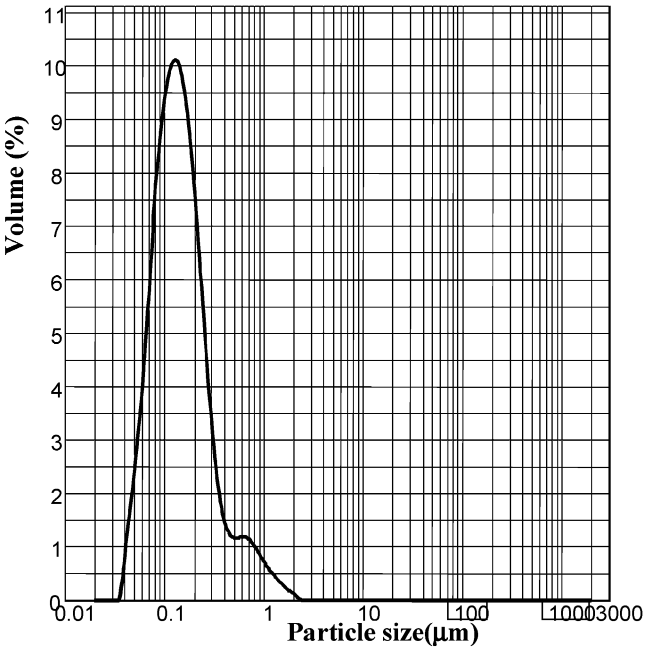


**Figure 7.** DLS analysis of PB particles synthesized by suspension ROMP of COD with amphiphilic NB−PS-*b*-PEO macromonomer **3b** (entry M, Table 2).

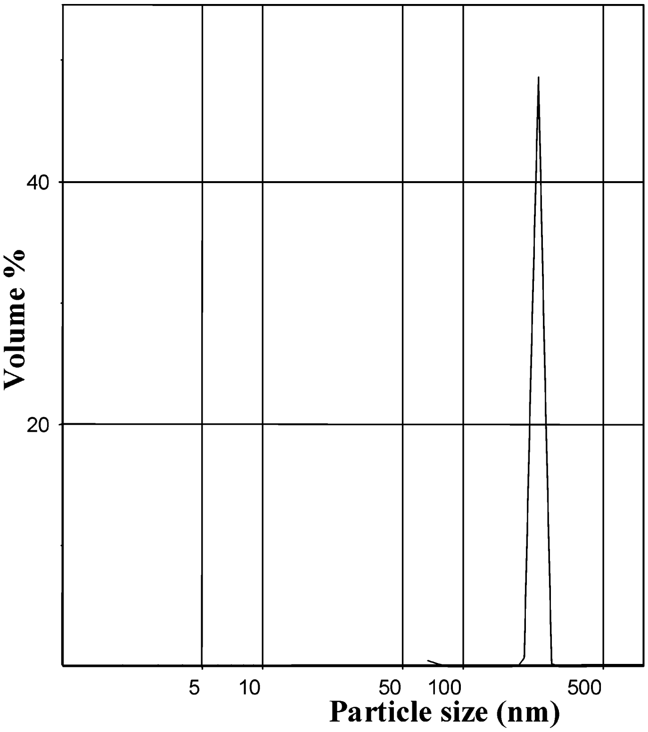


**Figure 8.** LALLS analysis of PB particles synthesized by suspension ROMP of COD with amphiphilic NB−PS-*b*-PEO macromonomer **3b** (entry M, Table 2).

As for the characterization of particles, a monodisperse population was observed by QELS with an average particle diameter of 150 nm (Figure 7). Similarly, SLS analysis (Figure 8) showed for the final suspension a quasi-monomodal size distribution with a majority of small particles with a size in the range of 150 nm. This size value is much smaller than that usually obtained by suspension polymerization. Such a difference suggests that the polymerization has occurred in another locus than the monomer droplets.

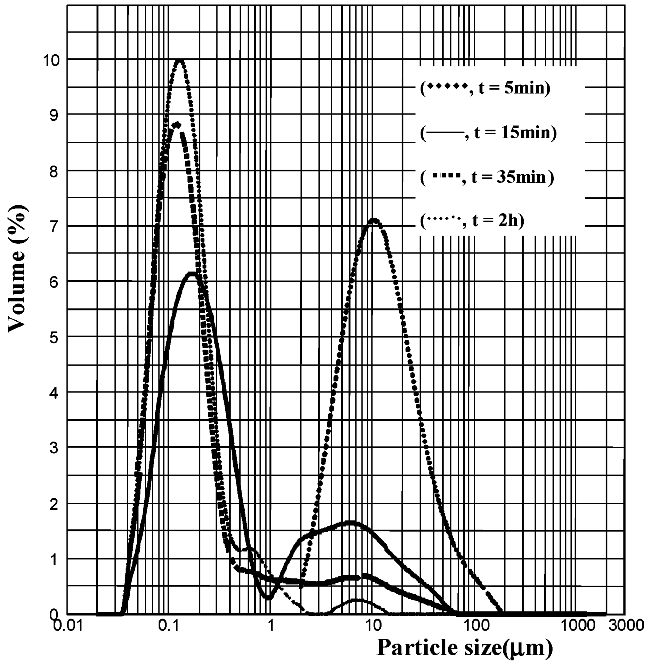


**Figure 9.** Variation of particle size vs time by DLS for suspension ROMP with amphiphilic NB−PS-*b*-PEO **3b** (entry M, Table 2).

The nucleation process was thus investigated by monitoring the variations of the particle sizes as a function of time (Figure 9). Within the first minutes of reaction, monomodal but broad in size population was visible in the micrometric size range (Dn = 11 $\mu$m). After 15 min of reaction, a second family of particles, smaller in size, appeared in the nanometric size range. The next hours of polymerization continued to favor the smallest population of about 150 nm diameter at the expense of those of larger size to such an extent that the size distribution became almost but not totally monomodal.

This demonstrates that two nucleation mechanisms occurred during polymerization: small particles can be assumed to derive from the PB-*g*-(PS−PEO) graft copolymer micelles or from micellar aggregates of **3b** more or less swollen by the monomer. As for the large size particles they have been more probably produced by the reaction occurring within the reservoir droplets, following the classical scheme of a suspension polymerization.

Owing to its addition mode (see experimental part), COD is probably first “forced” to react within the monomer droplets, leading to large particle sizes. The addition to water of surface active polymers possessing a nucleation activity has probably induced a second locus of polymerization, leading to the formation of smaller size particles.

**III. Suspension ROMP of 1,5-Cyclooctadiene in the Presence of a NB−PS−PEO Block Macromonomer (3a, 3b) as Stabilizer.** Instead of using of **1** as reactive stabilizer which eventually ended up with the particles’ flocculation, a second strategy consisted in using a block copolymer as macromonomer **3a** including a very short PS block ($\bar{M}_n$ = 500 g/mol) and a long PEO block ($\bar{M}_n$ = 10 100 g/mol) was carefully designed to exhibit both hydrophobicity and hydrophilicity without affecting its water solubility. It is indeed essential to avoid the formation of micellar aggregates (that could compete with the monomer droplets as reaction loci). The very weak diffusion properties of **3a** could be checked by DLS analysis. In the experiment N (entry N, Table 3), an organic solution containing **3a** and COD was introduced in water containing the suspending agent, causing a stronger turbidity compared to that observed when we used **1a** (entry E, Table 2). The polymerization was then triggered at 70 °C, and a stable colloidal suspension could be achieved after 3 h of reaction (procedure II, see experimental part). **3a** thus proved to be remarkably well-suited to stabilize the particles formed.

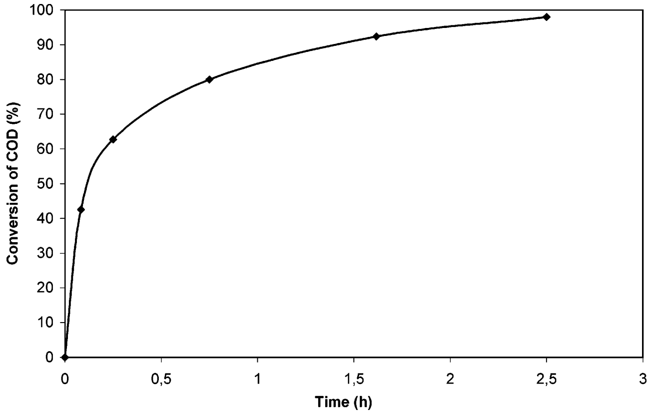


**Figure 10.** Conversion of 1,5-cyclooctadiene vs time for suspension ROMP in water in the presence of **3a** (entry N, Table 3).

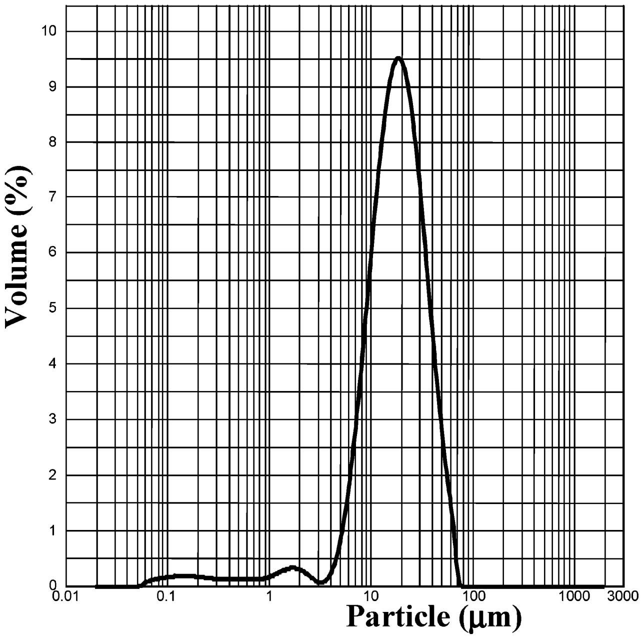


**Figure 11.** LALLS analysis of PB particles synthesized by suspension ROMP of COD water in the presence of **3a** (entry N, Table 3).

**III.1. Kinetic Results.** The experimental conversion curve of COD is given in Figure 10. As graphically shown, the monomer could be totally consumed in less than 3 h. The complete conversion and its high rate well support a polymerization occurring inside the monomer droplets.

**III.2. Suspension Characterization.** Figure 11 shows the distribution in sizes of the colloidal suspension stabilized by **3a**. A population with an average diameter of 19 $\mu$m is clearly observed by LALLS analysis. One has to stress that similar size values were also obtained by microscopy (Figure 12). The size range

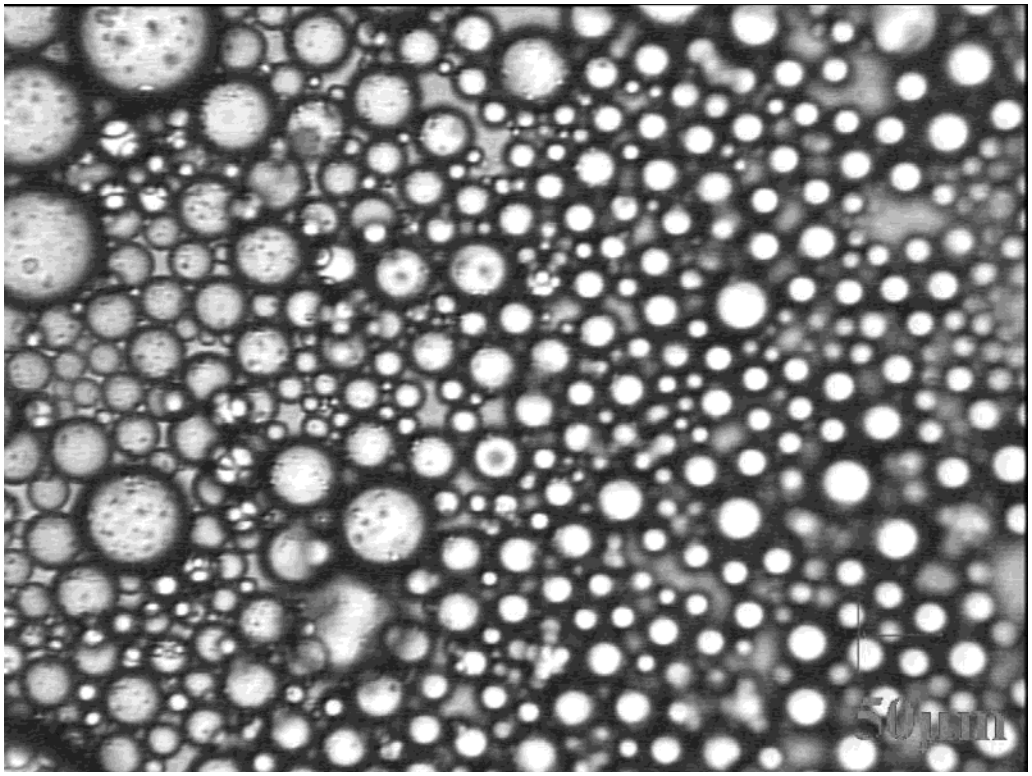


**Figure 12.** OM picture of PB particles synthesized by suspension ROMP of COD water in the presence of **3a** (entry N, Table 3).

indicates that these particles were produced via a mechanism of suspension polymerization. However, some particles in the nanometric size range were also detected (whose presence was definitively eliminated after filtration of the larger size particles). The surfactant properties of **3a** as well as those of amphiphilic species (PB-*g*-PS−PEO) that could be released from particles might be responsible for their formation.

In another experiment (entry O, Table 3), a NB−PS-*b*-PEO macromonomer **3b** exhibiting known surfactant properties was employed in order to examine the influence of micellar aggregates on the characteristics of the particles formed. As expected, the size distribution was considerably affected by the presence of such micelles: several populations of particles were obtained which is in agreement with a nucleation occurring not exclusively within the monomer droplets. The presence of secondary polymerization loci inside micelles resulted in significant changes in the conversion of COD as well. Compared to the suspension polymerization performed in the presence of **3a** (entry N, Table 3), the rate of consumption of the cycloolefin was significantly slower and remained incomplete with a limiting conversion of 42%. Such a difference is certainly the result of the partition of the COD between micellar aggregates and monomer particles whereas COD would have been stuck within the droplets in the absence of micelles (entry N, Table 3).

## Conclusion

In this work, stable 1,4-polybutadiene particles were prepared via the suspension ROMP of COD in water. Two strategies of stabilization have been successfully developed: both rest on the observation that an appropriate stabilizing agent must be at the same time hydrosoluble and possess a certain hydrophobicity so as to favor its localization at the particle surface and avoid its complete migration to the continuous phase. In this sense, NB−PS−PEO-type block copolymer and a graft copolymer PB-*g*-PEO proved to efficiently stabilize the polybutadiene particles formed. To our knowledge, this work represents the first example of synthesis of PB particles obtained by suspension ROMP.

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