

# Synthesis of latex particles by ring-opening metathesis polymerization

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## Abstract

This paper reviews the recent discoveries that were achieved by our group in the field of particle synthesis via ring-opening metathesis polymerization (ROMP). Both polynorbornene and polybutadiene-based particles were prepared by the respective ROMP of norbornene and cyclooctadiene initiated by  $(PCy_3)_2Cl_2Ru=CHPh$  using several methods of polymerization in dispersed media, such as dispersion, suspension and miniemulsion. Depending upon the process implemented, particles size was found to range from 300 nm to 20  $\mu m$ . © 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Ring-opening metathesis polymerization; Dispersion polymerization; Suspension polymerization

## 1. Introduction

Ring-opening metathesis polymerization (ROMP) has gained widespread interest over the last decades, both as a versatile method to synthesize unsaturated polymers of high potential, e.g. polybutadiene, and also as an innovative route to access to polymer microstructures which cannot be prepared by free-radical means, e.g. polynorbornene and polycyclooctene. As ROMP works via transition metal catalysis, most studies are usually carried out in bulk or in solution under anhydrous conditions. Little attention has been given so far to extend this reaction in dispersed media. If ROMP can be implemented in a dispersed medium, as it is extensively the case for radical polymerization, valuable polyalkenamers could be produced in the particle form with remarkable benefits in terms of applications and of polymerization process. The poisoning effect of polar and aqueous solvents toward catalyst can be regarded currently as the ground of such a limitation. Recently, the discovery by Grubbs of a new family of ruthenium-based carbene complexes retaining high activity in the presence of water has opened unexpected perspectives for the implementation of ROMP in dispersed media [1] (Fig. 1).

The first ROMP in dispersed medium were carried out by

Rinehart et al. [2] and Michelotti [3] as recently as 1965 using ruthenium, iridium and osmium based catalysts. Although these pioneering polymerizations suffered from very low yields, they were instrumental in proving that strained cycloolefins, such as norbornene and some of its derivatives could be polymerized in alcoholic or aqueous emulsion in presence of unreactive stabilizer. Meanwhile, Calderon et al. [4] introduced the term of ‘metathesis’ and demonstrated that carbon–carbon double bonds were broken throughout the ROMP reaction. Few years later, its mechanism [5] was finally elucidated and following this discovery, metalla-alkylidene (metalla-carbene) complex was clearly evidenced as the actual active species intervening in ROMP process (Scheme 1).

Subsequent efforts in catalyst design enabled significant improvements for applying ROMP in a dispersed medium. In 1993, Booth et al. [6] studied the dispersion ROMP of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene initiated by  $RuCl_3 \cdot 3H_2O$  in water: stable latexes of 100 nm were synthesized. In addition, Wache [7] described in 1995 the emulsion ROMP of norbornene initiated by two different water soluble catalysts based on Ru(IV) using sodium dodecyl sulfate as stabilizer. At the same period, a breakthrough occurred when alkylidene complexes based on ruthenium [8] were used directly as initiators. For the first time, it was possible to control ROMP reactions performed in the presence of water. More significantly for applications in dispersed media, these catalysts presented

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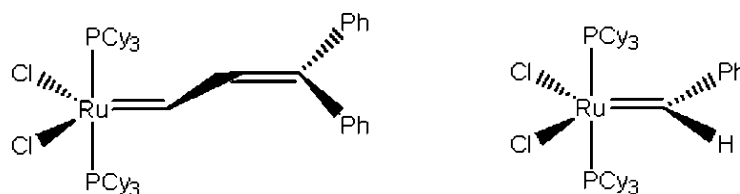


Fig. 1. Grubbs' Ruthenium-based carbene complexes.

the remarkable ability to be tolerant to protic functions while exhibiting a high activity. 'Living' polymerizations in water of hydrophilic and hydrophobic norbornene derivatives initiated by these novel initiators were thus described with an ionic stabilizer [9,10]. More recently, the synthesis of water soluble alkylidene catalysts [11,12] enabled researchers to study the emulsion polymerization of norbornene under 'living' conditions. Likewise, Claverie et al. [12] investigated the mini-emulsion ROMP of less strained cycloolefins (cyclooctene and cyclooctadiene). Unfortunately, low polymerization yields were obtained.

In a recent addition to this field, we have showed that  $\alpha$ -norbornenyl poly(ethylene oxide) macromonomer can efficiently stabilize latex particles synthesized by ROMP in a dispersed medium [13]. Unlike classical ionic and steric stabilizers, these reactive steric stabilizers present the advantage of being covalently bound onto the particle surface. In this way, one can prevent the stabilizer desorption under stress or its migration when filming latexes. Consequently, macromonomers can be regarded as efficient stabilizers to improve significantly the colloidal stability of latex particles.

This paper discusses our recent advances for implementing ROMP in a dispersed medium as an innovative method to prepare latex particles showing low polydispersity and very good stability. Three methods for applying ROMP in dispersed media are presented successively, including dispersion, suspension and miniemulsion polymerization. This contribution essentially focuses on the strategies devised by our group for the synthesis of particles based on polynorbornene (PNB) and polybutadiene (PB).

## 2. Experimental section

### 2.1. Materials

All reagents were dried, stored and used under inert atmosphere. ROMP reactions were carried out under inert atmosphere. Norbornene was stirred over sodium at 70 °C

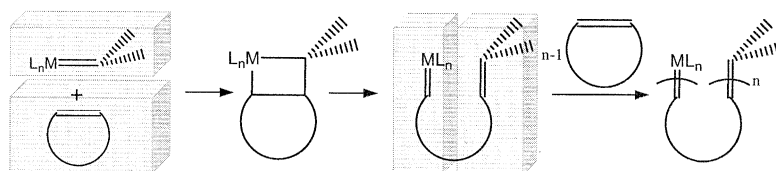
for 7 h and subsequently distilled. 1,5-cyclooctadiene (Aldrich) was kept over CaH<sub>2</sub> and then freeze vacuum distilled.  $\alpha$ -norbornenyl poly(ethylene oxide) macromonomer [14] (1), graft copolymers [15] (PB-g-PEO, 2),  $\alpha$ -norbornenyl polystyrene-*b*-poly(ethylene oxide) [16] (NB-PS-*b*-PEO, 3) and polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO, 4) have been prepared according to procedures described in the literature. Poly(diallyl methyl ammonium chloride) has an average molecular weight ranging from 200,000 to 350,000 g/mol.

### 2.2. Methods

Conversion of monomers (norbornene and 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 ( $\bar{M}_n = 1500 \text{ g mol}^{-1}$ ). The SEC equipment 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. The particle sizes were determined by static (SLS) or dynamic (DLS) light scattering, optical microscopy (OM) and transmission electron microscopy (TEM). A MASTER-SIZER instrument was used to study the particle size by SLS. DLS measurements were performed using a MALVERN zetasizer 3000 equipped with He-Ne laser. Before measurements, latexes were diluted about 100 times to minimize multiple scattering caused by high concentration. Particle sizes were also measured by OM using a Sony Laborlux microscope and by TEM using a JEOL JEM-2010 transmission electron microscope.

#### 2.2.1. Dispersion ROMP

Dispersion polymerizations were carried out at room temperature in a 100 mL glass reactor under inert atmosphere and stirring. In a typical synthesis, 20 mg ( $2.4 \times 10^{-5} \text{ mol}$ ) of catalyst was dissolved in 10 mL of dichloromethane/ethanol mixture (50/50% vs volume). Both monomer (norbornene or



Scheme 1. Metallacyclobutane mechanism.

cyclooctadiene) ( $8.1 \times 10^{-3}$  mol) and  $\alpha$ -norbornenyl poly(ethylene oxide) macromonomer (**1**), ( $\bar{M}_n = 4700$  g/mol,  $1.4 \times 10^{-4}$  mol) were first dissolved in 14 mL of dichloromethane/ethanol solution (35/65% vs volume) and added to the catalyst solution under nitrogen. The deactivation of the reaction medium was performed by addition of 0.1 mL of ethylvinylether.

### 2.2.2. Suspension ROMP

In a typical reaction, 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 a homogeneous mixing. 80 mL water containing 1% poly(diallyl methyl ammonium chloride) solution and 0.7 g of co-stabilizer (1, 2 or 3) 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 completed after  $\sim 2$  h when spherical polybutadiene beads were formed. The deactivation of the reaction medium was performed by addition of 0.1 mL of ethylvinylether.

### 2.2.3. Heterophase ROMP from miniemulsion droplets

In a typical recipe (Exp B-5, Table 3), 1.5 g of polystyrene-*b*-poly(ethylene oxide) (PS-PEO 4) surfactant ( $\bar{M}_{n,PS} = 1400$  g/mol;  $\bar{M}_{n,PEO} = 8700$  g/mol) are dissolved in 150 mL of ultrapure degassed water. In an argon filled drybox, Grubbs catalyst (360 mg, 0.44 mmol) is dissolved in a mixture of toluene (5 mL) and hexadecane (1.9 mL, 6.50 mmol). This purple solution is then added outside the drybox to the stabilizer water solution and stirred over 10 min. The miniemulsion is prepared by sonicating the mixture during 5 min at 60% amplitude (Sonic sonifier W750). The miniemulsion is then transferred under argon into the polymerization reactor heated at 80 °C. After 5 min of stirring (350 rpm), 15 g of pre-heated monomer (80 °C) are added dropwise to the miniemulsion. The initially purple mini-emulsion becomes light grey. The deactivation of the

reaction medium was performed by addition of 0.1 mL of ethylvinylether.

## 3. Results and discussion

### 3.1. Dispersion ROMP

Polynorbornene (PNB) and polybutadiene (PB)-based latex particles were first prepared by dispersion ROMP in a dichloromethane/ethanol mixture using a  $\alpha$ -norbornenyl poly(ethylene oxide) macromonomer (**1**) of 4700 g/mol as steric stabilizer and the ruthenium-based complex  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  as initiator. In any case, the particles can be viewed as a collection of graft copolymers PNB-*g*-PEO and PB-*g*-PEO maintained together through hydrophobic interactions and stabilized by the presence of PEO grafts onto their surface (Scheme 2).

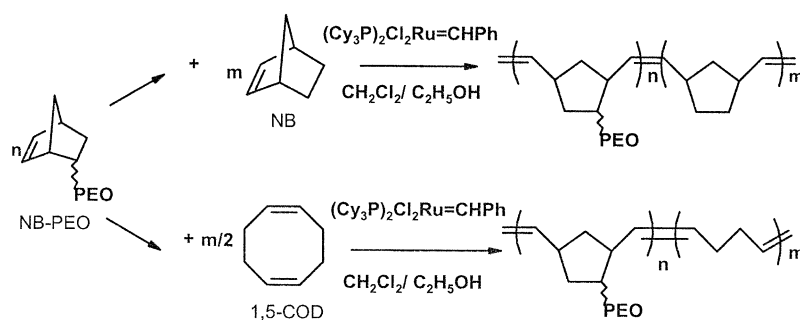
Under similar conditions of reaction, the kinetics of polymerization and the characteristics of the particles formed were found totally different for the two kinds of monomer.

#### 3.1.1. Dispersion ROMP of norbornene (NB)

As reported in our first study [13], the dispersion was formed at the early stage of polymerization. The conversion curves of NB and macromonomer **1** vs time are shown in Figs. 2 and 3. The rate of consumption of monomer was found to be considerably higher than that of the macromonomer (**1**). As illustrated graphically, norbornene was totally consumed after 5 min of reaction whereas only 10% of the PEO macromonomer reacted.

Three reasons may be advanced to account for such a difference of reactivity: firstly, the macromonomer chains carry terminal unsaturations that are poorly accessible to active species, secondly their concentration in the reaction medium remains low in comparison with that of norbornene, and finally there is an increasing incompatibility between them and the polymeric chains formed throughout the reaction [17].

Consequently, there is a strong tendency to ‘blockiness’ for the final polymer microstructure in such a



Scheme 2. Dispersion ROMP reaction of 1,5-cyclooctadiene (COD) and norbornene (NB) in the presence of a  $\alpha$ -norbornenyl poly(ethylene oxide) macromonomer (NB-PEO, **1**).

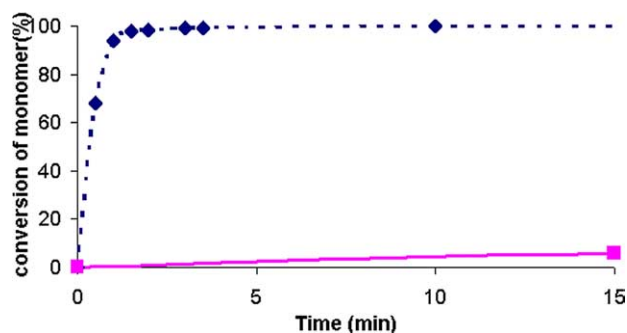


Fig. 2. Conversion of 1,5-cyclooctadiene (■, COD) and norbornene (◆, NB) versus time for their dispersion ROMP in  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  (42/58% vs volume). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

copolymerization involving a PEO macromonomer. A gradient-type graft copolymer is thus formed in this case, containing at first very few PEO grafts at one end and progressively more and more to become an almost pure comb-type polymer at the other end.

The average particle size is in the order of 400 nm and one has to stress the good agreement between size values obtained by transmission electron microscopy ( $D_n(\text{TEM}) = 420 \text{ nm}$ ) and dynamic light scattering ( $D_n(\text{DLS}) = 440 \text{ nm}$ ). TEM micrograph of latex (Fig. 4) shows particles exhibiting rather regular spherical shape and monomodal distribution.

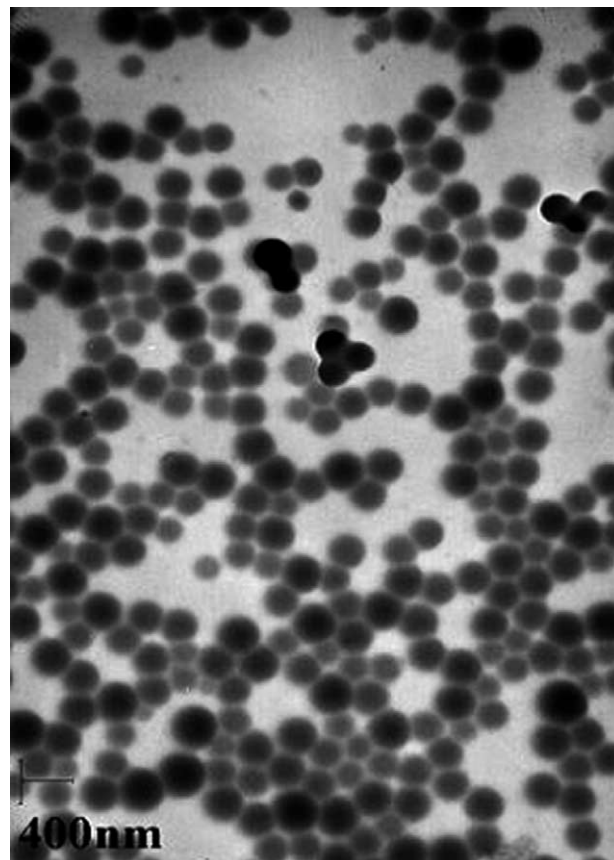


Fig. 4. TEM picture of PNB latexes synthesized by dispersion ROMP of NB.

### 3.1.2. Dispersion ROMP of 1,5-cyclooctadiene (COD)

When NB was replaced by a cycloolefin of lower ring strain, such as COD (all other parameters being kept constant), the macromonomer 1 displayed in this case a much faster rate of incorporation than that of the monomer: 80% of 1 was consumed after 1 h whereas only 10% of COD reacted (Figs. 2 and 3). The high reactivity of the norbornenyl end group can be seen as the driving force allowing the rapid incorporation of 1. Though they showed a significant difference in their respective reactivity, both macromonomer and COD could not be polymerized until

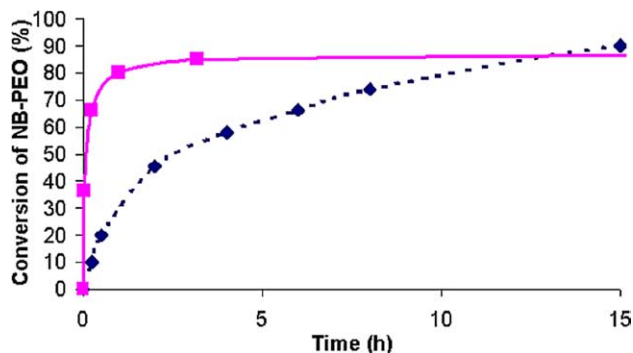


Fig. 3. Conversion-time curve of PEO macromonomer during its dispersion copolymerization with 1,5-cyclooctadiene (■) and norbornene (◆) in  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  (42/58% vs volume). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

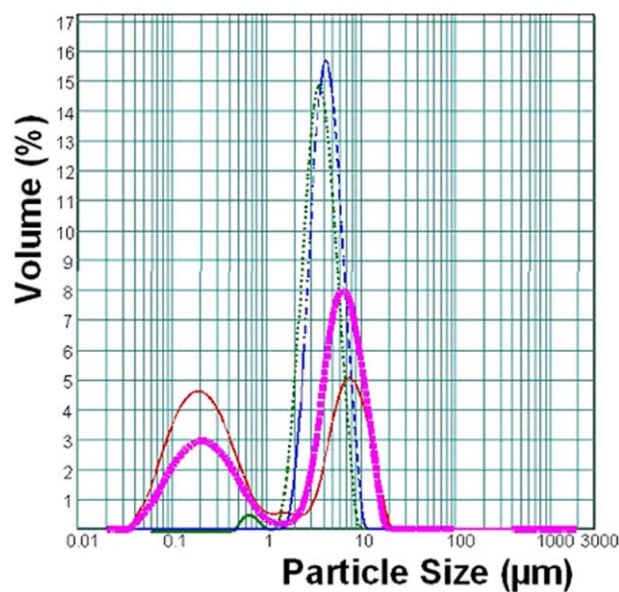


Fig. 5. Variation of particle size versus time by DLS for dispersion ROMP of COD in  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  (42/58% vs volume): ( $t = 2 \text{ h}$ , ● ● ●), ( $t = 4 \text{ h}$ , - - -), ( $t = 7 \text{ h}$ , ■ ■ ■), ( $t = 20 \text{ h}$ , ■ ■ ■ ■). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

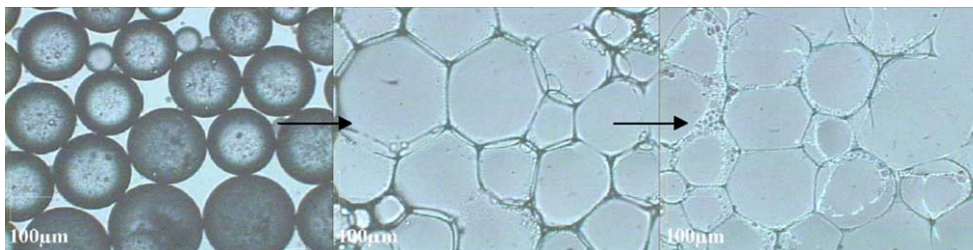


Fig. 6. OM pictures of aggregation of PB particles synthesized by suspension ROMP of COD without co-stabilizer.

completion: the conversion of macromonomer was about 85% after 2 h of reaction and that of COD reached 60% after two days of reaction. As discussed in a previous contribution [18], the slower conversion of COD compared to 1 has also an impact on the onset of turbidity. The first signs of opalescence can be observed only after 1 h 30 of polymerization and the first particles are characterized after 2 h of reaction (Fig. 5). A broadly distributed population of particles is first formed, ranging from 2 to 10  $\mu\text{m}$ . A second family of particles, smaller in size and polydisperse, then appears after about 7 h of reaction (Fig. 5). In contrast to the first population of particles formed during the initial hours of reaction, this latter comprises irregular and non-spherical particles. Such a difference in particle morphology was attributed to a lower and insufficient PEO grafting density onto the newly-formed particles surface [19]. Regarding the second population of particles, reshuffling reactions that are proved to occur extensively within the particles can explain its late appearance. These degradation reactions release some PEO-rich species outside the particle that are able to nucleate subsequently.

In order to produce monomodal latex of polybutadiene, some polymerizations were performed using low COD concentration. Although one population was characterized under such particular conditions, this strategy had the undesirable effect to produce a high fraction (60%) of soluble copolymers.

### 3.2. Suspension ROMP of 1,5-cyclooctadiene (COD)

For this second study, COD was polymerized for the first time by suspension ROMP. In a typical process, the monomer has to be dispersed as droplets through vigorous stirring (600 rpm) in an aqueous phase including a suspending agent. In this study, a poly(diallyl methyl ammonium chloride) known to provide an efficient electrosteric stabilization was used. The polymerization was then initiated at ambient temperature by addition of an organic solution of  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$ . Due to the initiator's solubility in the monomer phase, the polymerization is likely to proceed within the droplets, these latter converting into polymer particles as reaction takes place. After two hours of reaction, jelly-like PB beads were generated. However, these latter appeared poorly stabilized and the cessation of agitation caused a slow aggregation (Fig. 6). Nonetheless, a complete conversion of COD was reported, suggesting the promising activity of the ruthenium-alkylidene  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  in water.

In a view to prevent flocculation of the polybutadiene beads, a co-stabilization was contemplated. Various stabilizers based on PEO have been tried subsequently, including poly(ethylene oxide) macromonomer (NB-PEO) (1), graft copolymers (PB-*g*-PEO) (2),  $\alpha$ -norbornenyl polystyrene-*b*-poly(ethylene oxide) macromonomer (NB-PS-*b*-PEO) (3). In a view to compare their respective efficiency, the

Table 1  
Characteristics of 1,4-polybutadiene particles stabilized by a suspending agent and co-stabilizer (1, 2, 3)

Stabilizer	NB-PEO (1)	NB-PEO (1)	NB-PEO (1)	PB- <i>g</i> -PEO (2)	NB-PS- <i>b</i> -PEO (3)
Weigh of stabilizer (g)	0.7	0.7	0.7	0.7	0.7
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 ( $^{\circ}\text{C}$ )	25	50	70	70	70
System stability	Slow coagulation	Slow coagulation	Slow coagulation	Stable	Stable
Dn(SLS) ( $\mu\text{m}$ )	–	–	–	10	19
Dn(OM) ( $\mu\text{m}$ )	–	–	–	–	19.2
COD conversion (wt%)	100	100	100	100	100
PEO content of particles (wt%) <sup>a</sup>	6	9	10	46	100

<sup>a</sup> Determined by NMR.

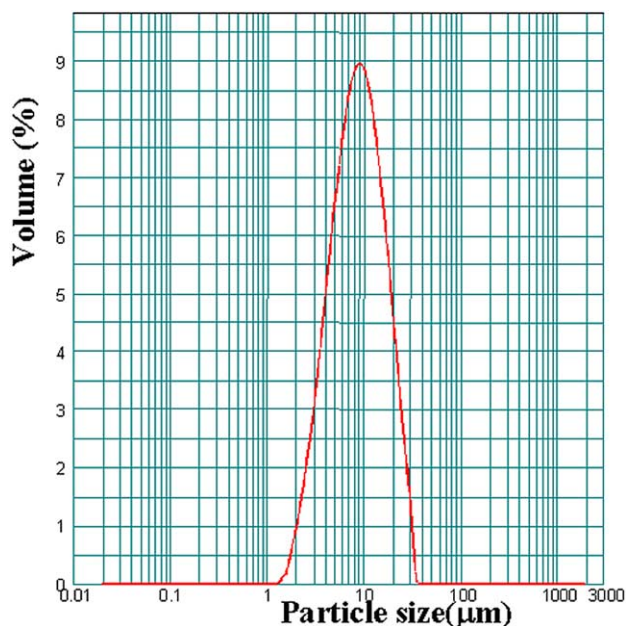


Fig. 7. SLS analysis of PB particles synthesized by suspension ROMP of COD with **2** as stabilizer.

different co-stabilizers were carried out while keeping all other parameters unchanged.

All latexes obtained have been characterized by the use of SLS and OM.

Our first attempts to use  $\alpha$ -norbornenyl poly(ethylene oxide) macromonomer **1** as co-stabilizer led to a slow coagulation. The SEC analysis showed that only 6% of **1** were actually converted into the bead form and were thus available for the stabilization of the particles formed (Table 1). The rest kept either unreacted in water or incorporated into soluble PEO-rich graft copolymers because of the strong hydrophilic character of macromonomer chains.

In order to minimize the hydrosolubility of **1**, COD was polymerized at higher temperatures. An increase in reaction temperature is expected to have a beneficial effect on the

macromonomer conversion by dissociating the hydrogen bonds existing between the ethylene oxide groups and water. Consequently, PEO chains should be driven out of the aqueous phase and enter more easily into the particles. Unfortunately, experiments performed at 50 and 70 °C led to precipitation. (Table 1).

A stable colloidal suspension of polybutadiene particles was successfully reported when a graft copolymer (PB-*g*-PEO) **2** was introduced in the reaction medium (Table 1). Its analysis by SLS showed a monomodal but wide size distribution ranging from 3 to 20  $\mu\text{m}$  (Fig. 7). In addition, a complete consumption of COD was observed after 2 h of reaction.

The particles obtained are much lower than in free-radical initiated suspension polymerization (for this latter, size values are typically comprised between 20 and 1000  $\mu\text{m}$ ). This may be attributed to the PEO chains covalently grafted onto the particle surface whereas conventional suspension most often involves surfactant adsorbed to the surface. The Fig. 8 displays an OM picture of these polybutadiene-based particles, appearing spherical and well-stabilized.

The last strategy has consisted in using a block macromonomer instead of a hydrophilic one. Macromonomer stabilizers (NB-PS-*b*-PEO, **3**) including a very short PS block ( $\bar{M}_n = 500$  g/mol) and a long PEO block ( $\bar{M}_n = 10, 100$  g/mol) were carefully designed to provide an additional hydrophobicity compared to that of their hydrophilic analogues (**1**) without too much affecting their water solubility in order to avoid the formation of micellar aggregates. The polymerization was triggered at 70 °C. After 3 h of reaction, NB-PS-*b*-PEO and COD were totally consumed and a stable colloidal suspension could be obtained (Table 1). Block macromonomer **3** thus proved to be remarkably well-suited to stabilize the particles formed. Latex particles with an average diameter of 19  $\mu\text{m}$  were clearly characterized by OM analysis (Fig. 9). One has to stress that similar size values were also obtained by microscopy (Table 1). The size range well indicates that

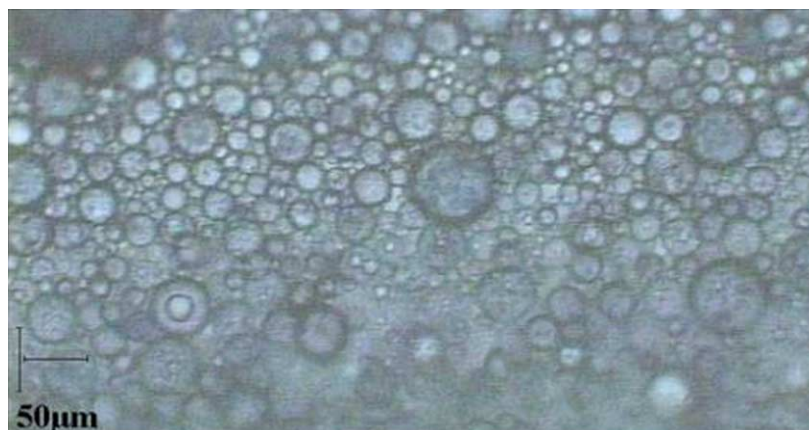


Fig. 8. OM picture of PB-based particles synthesized by suspension ROMP of COD with **2** as stabilizer.

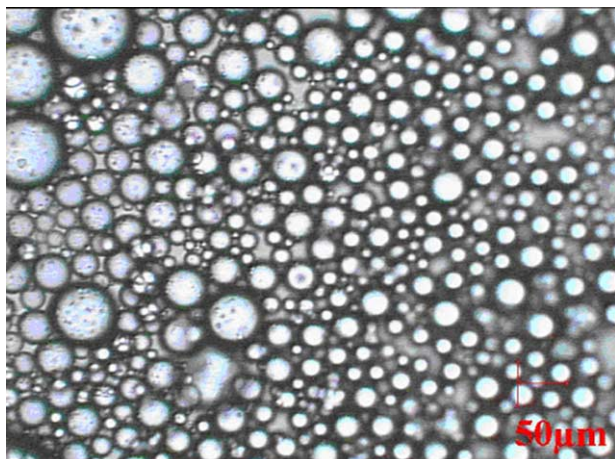


Fig. 9. OM picture of PB latexes synthesized by suspension ROMP of COD with **3** as stabilizer.

these particles were well produced via mechanism of suspension polymerization. However, some particles in the nanometric size range were also detected. These latter might result from micellar nucleation due to the surfactant properties of amphiphilic species (PB-*g*-PS-PEO) that are continuously released from particles.

In this work, stable 1,4-polybutadiene particles were prepared via suspension ROMP of COD in water. To be effective, a co-stabilizer agent must be hydrosoluble but possess a certain hydrophobicity so as to promote its presence at the particle surface and thus avoid a complete solubilization in the continuous phase. In this sense, a block macromonomer of NB-PS-PEO-type and a PB-*g*-PEO graft copolymer have proved to efficiently stabilize the polybutadiene particles formed.

Table 2  
Characteristics of PNB and PB latexes from ROMP miniemulsion via first route

Monomer	[Monomer] (g/L)	[PS-PEO 1] (g/L)	$V_{\text{toluene}}$ (mL)	[NB]/[cat.]	$T$ (°C)	Coagulation (%)	Conv. (%)
NB	100	100	0.2	2119	20	100	100
NB	100	100	0.3	2119	5	100	100
NB	100	10	1	2330	20	100	100
NB	100	25	1	17,480	20	100	100
NB	100	25	1	17,480	80	100	100
COD	120	10	1	17,480	80	0	10
COD	60	25	1	2119	80	0	5
COD	50	25	1	2119	80	0	5

Table 3  
Characteristics of PNB and PB latexes from ROMP miniemulsion via second route

Monomer	Rate of monomer addition (mL/h)	[Monomer] (g/L)	$V_{\text{THF}}$ (mL)	$T$ (°C)	Coagulation (%)	$D_p$ (nm)	Conv. (%)
NB	1	100	0	80	40	390	100
NB	1	100	4	80	45	450	100
NB	1	100	4	60	65	340	100
COD	0.5	100	0	80	0	500	85
COD	0.5	50	0	80	0	410	90

### 3.3. Heterophase ROMP from miniemulsion droplets

In this last work, NB and COD were polymerized under miniemulsion conditions. Miniemulsions are submicron dispersions of monomers in water stabilized by a surfactant and an oil-soluble agent added in order to avoid Ostwald ripening. Free-radical miniemulsion polymerization has been extensively investigated, using typically oil soluble initiators dissolved in the monomer prior to the miniemulsification step. Owing to the high reactivity of  $(\text{PCy}_3)_2\text{-Cl}_2\text{Ru}=\text{CHPh}$  at ambient temperature, a similar procedure cannot be transferred to ROMP. Therefore, two alternative strategies of miniemulsion polymerization were devised. In the first one, the catalyst solution was introduced to a miniemulsion of monomer. In the second one, the monomer is added continuously to the reaction medium after miniemulsification of the catalyst solution. In both cases, a polystyrene-*b*-poly(ethylene oxide) (PS-PEO **4**) ( $\bar{M}_{n,\text{PS}} = 1400$  g/mol;  $\bar{M}_{n,\text{PEO}} = 8700$  g/mol) was used as stabilizer.

### 3.4. First route

In a first series of experiments (Table 2), the catalyst dissolved in toluene was added to a stable norbornene miniemulsion (Fig. 10).

All attempts led to a rapid coagulation in less than 5 min of reaction. This result can be explained by the strong hydrophobicity of the catalyst solution. Once introduced in the reaction medium, the catalyst forms large and poorly-stabilized droplets that destabilize the monomer miniemulsion. Norbornene diffuses from small droplets to the larger

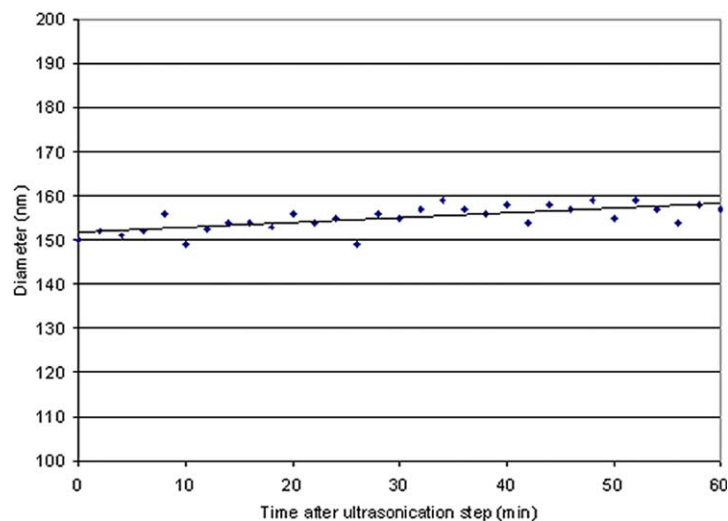


Fig. 10. Stability of the NB miniemulsion versus time.

catalyst ones where polymerization actually occurs. Insufficiently stabilized polymer particles are formed, leading to a rapid coagulation. In addition, destabilization of miniemulsions can also occur by collision and coalescence processes.

In order to overcome this issue, various experimental parameters have been reviewed such as the stabilizer concentration, the temperature and the amount of toluene but without success.

Considering the miniemulsion polymerization of COD, a similar destabilization process is suspected to take place (Table 2). However, the fairly lower reactivity of this monomer compared to NB leads to weak conversion rates (<10%) that prevent the system from a global coagulation.

### 3.5. Second route

The second strategy consists in using a miniemulsion of catalyst, to which a solution of monomer dissolved in THF is fed continuously. The results obtained under different experimental conditions are given in Table 3.

Under this method, NB can be polymerized until completion. In addition, latex particles in the hundred nanometric size range were generated. The final particle size is larger than that of the initial catalyst droplets, attesting to the progressive diffusion of monomer into the catalyst droplets. However, a large amount of coagulum ranged from 40 to 65% depending on the formulation used was also observed. There are two possible explanations for this. Firstly, the partial diffusion of catalyst through the aqueous phase can cause a latex destabilization. Nevertheless, the high hydrophobic behaviour of the Grubbs catalyst makes this hypothesis improbable. Secondly, the hydrophobic behaviour of NB could prevent it from diffusing easily through aqueous phase and then urges the NB to form large droplets. Destabilisation of emulsion could occur by collision/coalescence processes with catalyst droplets.

In contrast to NB, less strained COD could be polymerized under a similar miniemulsion procedure without any occurrence of coagulation even when high conversion rates were reached (Table 3). This result can be explained by the lower reactivity of COD which allows the re-organization of miniemulsion upon contact with COD prior to ROMP occurred. Particles obtained exhibited narrow size distribution and rather good stability attesting that PS-*b*-PEO copolymer can behave as an effective stabilizer in this case (Fig. 11). Ongoing work now focuses on the opportunity to stabilize the particles with NB-PS-*b*-PEO (**3**) macromonomer.

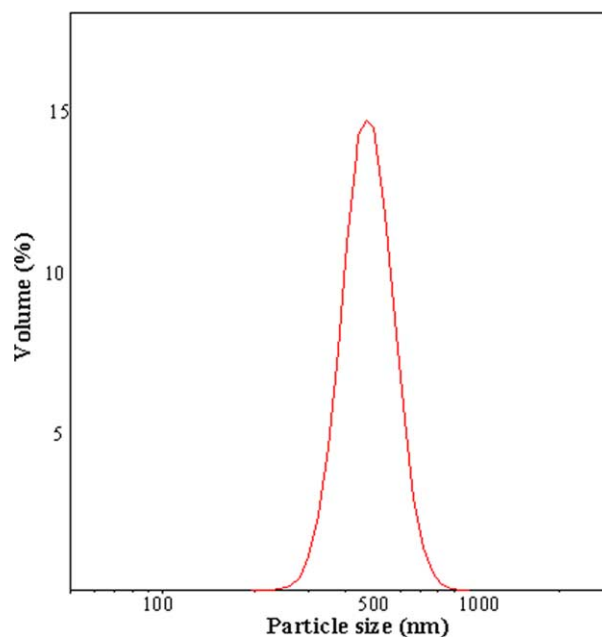


Fig. 11. DLS analysis of PNB particles synthesized by miniemulsion ROMP of NB.



#### 4. Conclusion

It was shown that the dispersed media process can be applied to the ROMP of cycloolefins. In dispersion ROMP, PNB and PB particles were synthesized using  $\alpha$ -norborne-nyl poly(ethylene oxide) macromonomer. Spherical and monodisperse PNB particles were obtained in the 400 nm size range. Broad particle size distribution was observed for PB particles with sizes ranging from 50 nm to 10  $\mu$ m, which were attributed to a prolonged nucleation period. In suspension ROMP, stable PB particles were obtained with either a graft copolymer PB-*g*-PEO or a PS-*b*-PEO macromonomer as stabilizer. Results obtained in miniemulsion ROMP are not so decisive and must be complete. Nevertheless, this first work encourages us to follow in this field. Besides, to our knowledge this study represents the first example of synthesis of latex particles obtained by ROMP in the presence of PS-PEO stabilizer.

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