Dispersion Ring-Opening Metathesis Polymerization of Norbornene Using PEO-Based Stabilizers

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ABSTRACT: Polynorbornene-based latex particles were prepared via dispersion ring-opening metathesis polymerization (ROMP) of norbornene (NB) in dichloromethane/ethanol medium and in the presence of a α-norbornenyl poly(ethylene oxide) macromonomer (NB−PEO). Colloidal dispersions in the 200−600 nm size range were obtained and characterized by electron microscopy and dynamic light scattering. This paper also investigates the reaction parameters that influence both the structure of the PNB-*g*-PEO graft copolymer formed and the characteristics of the resulting latex. In particular, the effect due to the macromonomer—its structure, concentration, and molar mass—and also the role respectively played by the medium polarity, the monomer concentrations, and initiator concentrations are discussed. The mode of addition of norbornene was also investigated. Attempts to synthesize pure polynorbornene latex particles are also described using either unreactive PEO-based stabilizers or PNB-*g*-PEO seeds.

Introduction

Little attention has been given so far to the potentialities offered by ring-opening metathesis polymerization (ROMP) as a means to synthesize latex particles. Very few studies addressing ROMP in dispersed medium have been indeed reported in the literature. For long, one major limitation was the sensitivity of the catalysts to polar and protic functions. Recently, the scope of ROMP has considerably expanded with the development of a new generation of initiators based on late transition metals that are remarkably tolerant of protic media and polar functions. ROMP can now be applied to a variety of conditions, including functional monomers and polar solvents, and still exhibits a “living” character.

In 1965, Rinehart and al.[1] were the first to describe the emulsion polymerization of norbornene using iridium- and ruthenium-based catalysts. More recently, Grubbs and al.[2] investigated the ROMP of 7-oxanorbornene derivatives in water. The same class of monomers was also polymerized under dispersion conditions by Lu and al.,[3] who used a conventional ruthenium trichloride complex: a stable dispersion could be obtained in the presence of a steric surfactant. However, the catalytically active species arising from these late transition metals were ill-defined and could not be identified. Subsequently to these earlier efforts, Grubbs[4,5] and co-workers developed a novel family of ruthenium-based carbene complexes that not only were tolerant of aqueous media but also could induce a “living” polymerization. Functionalized norbornene could be homopolymerized in water using a cationic surfactant and these ruthenium complexes. In a recent addition, Grubbs and al.[6] moved forward by proposing new water-soluble ruthenium−alkylidenes that were shown efficient as initiators for emulsion ROMP. Claverie and al.[7] also contributed to this subject by discussing the conditions to apply in the emulsion ROMP of norbornene (NB) using these new water-soluble Grubbs catalysts. Despite these developments, the ring-opening metathesis polymerization of hydrophobic cycloolefins in heterogeneous medium is still in its infancy. This lack of understanding prompted us to examine more closely the dispersion ROMP of norbornene in protic and organic medium.

We recently reported the synthesis of polynorbornene-based latex particles[8] by ROMP in dichloromethane/ethanol medium. A α-norbornenyl poly(ethylene oxide) macromonomer (NB−PEO, **1**) was used as stabilizer, the polymerization being initiated by a well-defined ruthenium metallaalkylidenic complex $(PCy_3)_2Cl_2Ru{=}CHPh$, known to retain its reactivity in protic solvents. Such a dispersion polymerization starts as a clear and homogeneous solution containing the monomer (here norbornene), the initiator, and the stabilizer, which eventually turned into a colloidal dispersion upon formation of polynorbornene (PNB). To our knowledge, it was the first report on latex particles obtained by ROMP dispersion in the presence of a macromonomer. Latex synthesized under these conditions are actually comprised of polynorbornene-*g*-poly(ethylene oxide) (PNB-*g*-PEO) graft copolymers sterically stabilized by the PEO part.

The present study focuses on the parameters that influence the colloidal properties of such dispersions stabilized by a reactive stabilizer. It also investigates the impact of the conditions used on the structure of the graft copolymer formed:

•The medium polarity, the initiator and monomer concentrations, the type of macromonomer, its molar mass, and concentration are the parameters that were varied and discussed in the light of the characteristics of the particles formed.

•The mode of addition of monomer—either performed at once or performed slowly throughout the polymerization—is another parameter that was investigated in regard to colloidal properties of the particles formed.

In a second part, attempts were made to prepare latex particles of pure polynorbornene, using various unreactive steric stabilizers based on PEO (**2**, **3**, **4**, **5**, and **6**, Table 1). The difficulties encountered with such a class of stabilizers prompted us to use a preformed seed of PNB-*g*-PEO latex and polymerize NB in their pres-

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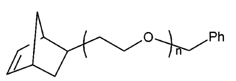
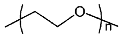
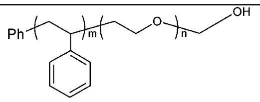
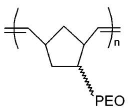
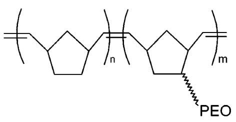
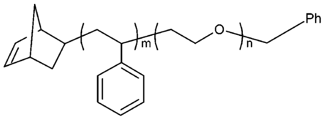
Table 1. Series of PEO-Based Steric Stabilizers

STABILIZERS	NUMBER	STRUCTURE
NB-PEO n=107, $\overline{M}_n$=4700*g*/*mol* n=170, $\overline{M}_n$=7500*g*/*mol*	1	
PEO *n=107*, $\overline{M}_n$=4700*g*/*mol*	2	
PS-PEO n=107, $\overline{M}_n$=4700*g*/*mol* m=120, $\overline{M}_n$=12500*g*/*mol*	3	
BRIJ	4	$C_{17}H_{38}$-(CH_2-CH_2-O)$_{100}$ -OH
PEO polymacromonomer $\overline{M}_{nGPC}$=52000*g*/*mol*	5	
PNB-g-PEO $\overline{M}_{nGPC}$=120000*g*/*mol*	6	
NB-PS-b-PEO n=116, $\overline{M}_n$=5100*g*/*mol* m=16, $\overline{M}_n$=1700*g*/*mol*	7	

ence. Characteristics of such PNB particles are also discussed and commented on.

Experimental Section

Materials. All reagents were dried, stored, and used under inert atmosphere. ROMP reactions were carried out under inert atmosphere. The ruthenium-based complex $(PCy_3)_2Cl_2Ru{=}CHPh$ was prepared following literature methods.[9] The α-norbornenyl poly(ethylene oxide)[10] macromonomer (**1**) and the α-norbornenyl poly(styrene-*b*-ethylene oxide)[11] (**7**) macromonomer have been prepared according to procedures described in the literature. Poly(ethylene oxide) lauryl ether (**4**), BRIJ (Aldrich), was used as received. As previously described,[10] the PEO polymacromonomer (**5**) was obtained by ROMP of a α-norbornenyl poly(ethylene oxide) macromonomer (**1**) using a Schrock-type molybdenum alkylidene complex $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr_2C_6H_3)(OCMe(CF_3)_2)_2$. **5** was used afterward as a stabilizer for the latex particles. The stabilizer **6** was synthesized by solution ROMP of a norbornene/**1** mixture (25/75 w/w) in CH_2Cl_2 using $(PCy_3)_2Cl_2Ru{=}CHPh$ as initiator. The resulting PNB-*g*-PEO graft copolymer (**6**) was used as a polymeric stabilizer.

Methods. The conversion of norbornene was determined by gas chromatography with a trace of undecane as internal standard. Conversion of macromonomer was monitored by size exclusion chromatography (SEC) using polystyrene as internal standard ($\bar{M}_n$ = 1500 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 dynamic light scattering (DLS) and transmission electron microscopy (TEM). 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 scatterings caused by high concentration. TEM pictures were performed with a JEOL JEM-2010 transmission electron microscope. The polydispersity index (PDI) and the particle diameter were determined over a great number of particles (at least 200 particles). The thermal analysis was performed with a Perkin-Elmer DMA instrument at a heating rate of 10°C/min and at 1 Hz frequency.

Batch Dispersion Polymerization. Dispersion polymerizations were carried out at room temperature in a 100 mL glass reactor under inert atmosphere and stirring. In a typical synthesis (entry A1, Table 2), 20 mg (2.4×10^{-5} mol) of catalyst was dissolved in 10 mL of dichloromethane/ethanol mixture (50/50% vs volume). Both norbornene (8.1×10^{-3} mol) and polymeric stabilizer (1.4×10^{-4} mol) were first dissolved in 14 mL of dichlomethane/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 ethyl vinyl ether.

Seeded Dispersion Polymerization. A seed latex was produced by dispersion polymerization under the conditions given above. These seeds were used after 48 h, the time for the active species present to decompose. Then, new charges of initiator (7.8×10^{-6} mol) and norbornene (2.6×10^{-3} mol) were successively introduced in the reaction vessel including the seed dispersion, the solid content being kept constant throughout the process.

Semibatch Dispersion Polymerization. A typical run was as follows (entry I, Table 3). First, 20 mg (2.4×10^{-5} mol) of catalyst was dissolved in 5 mL of dichloromethane/ethanol mixture (50/50% vs volume). The PEO macromonomer (**1**) (1.4×10^{-4} mol), dissolved in 7 mL of dichlomethane/ethanol solution (35/65% vs volume), was then added to the catalyst solution under nitrogen. A charge of norbornene (8.1×10^{-3} mol) dissolved in 12 mL of CH_2Cl_2/EtOH mixture(42/58 vs volume) was slowly added to the above reaction medium, over a period of 1 h. The deactivation of the reaction medium was performed by addition of 0.1 mL of ethyl vinyl ether.

Results and Discussion

(I) Dispersion Polymerization of NB in the Presence of a Reactive Stabilizer. To be effective in aqueous or polar medium, a nonionic emulsifier whose role is to stabilize latex particles by steric repulsion must contain the following: (1) a hydrophobic "anchoring" block with an affinity for the polymer particle surface; (2) a solvent-soluble segment that can prevent the particle from coagulating.

Amphiphilic block and graft copolymers based on PEO are the preferred nonionic stabilizers for particles formed in water and polar media. Such steric stabilization can also be generated "in situ" during the dispersion polymerization upon copolymerization of a PEO-based macromonomer with the hydrophobic monomer. In the latter case, the macromonomer can actually be viewed as a reactive stabilizer and the particles formed are comprised of graft copolymers bearing PEO side chains. In our case, macromonomers of PEO fitted with a norbornenyl unsaturation were used to stabilize the particles produced by ROMP of NB and thus prevent their flocculation.

I.a. Norbornenyl Poly(ethylene oxide) Macromonomer As Reactive Stabilizer. The dispersion ROMP of norbornene was performed in a dichloromethane/ethanol mixture using **1** as stabilizing agent (Scheme 1). The dispersion was formed at the early stage of polymerization and the macromonomer **1** proved to be remarkably well-suited to stabilize the particles formed in such a medium. The copolymerization of macromonomer **1** with norbornene indeed yielded PNB-*g*-PEO graft copolymers that were insoluble in the dichloromethane/ethanol mixture but instead afforded particles of nanometric size. Other authors have de-

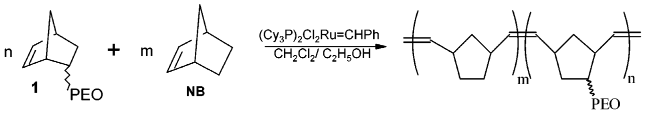
Table 2. Influence of Several Reaction Parameters on the Particle Size and the Size Distribution (Batch Process)

expts	$\bar{M}_n$(stabilizer), g/mol	stabilizer, g	[stabilizer]/[I]	NB, g	[NB]/[I]	I, mg	EtOH, mL	CH_2Cl_2, mL	D_n(TEM), nm	D_n(DLS), nm	PDI(TEM) D_w/D_n
A1	4700 (**1**)	0.658	5.8	0.763	337.5	20	14	10	420	440	1.07
A2	6800 (**7**)	0.658	5.8	0.763	337.5	20	14	10	318	387	1.10
B	7500 (**1**)	0.658	5.8	0.763	337.5	20	14	10	323	350	1.04
C	4700 (**1**)	0.329	2.9	0.763	337.5	20	14	10	515	586	1.10
D	4700 (**1**)	1.316	11.7	0.763	337.5	20	14	10	202	240	1.10
E	4700 (**1**)	0.658	5.8	0.763	337.5	10	14	10	340	387	1.05
F	4700 (**1**)	0.658	5.8	0.3815	169	20	14	10	240	260	1.17
G	4700 (**1**)	0.658	5.8	0.763	337.5	20	10	14	409	470	1.02
H	4700 (**1**)	0.658	5.8	0.763	337.5	20	18	6	248	345	1.08

Table 3. Effects of Batchwise and Influence of Several Reaction Variables upon the Particle Size and the Size Distribution in a Semibatch Procedure

expts	batchwise	$\bar{M}_n$(NB−PEO), g/mol	NB−PEO, g	NB, g	I, mg	EtOH, mL	CH_2Cl_2, mL	D_n(TEM), nm	D_n(DLS), nm	PDI(TEM) D_w/D_n
A1	batch	4700	0.658	0.763	20	14	10	420	440	1.07
I	semibatch	4700	0.658	0.763	20	14	10	230	100	$\gg 1$
J	semibatch	4700	0.658	0.763	20	18	6	155	70	1.12
K	semibatch	4700	0.1645	0.763	20	14	10	265	185	1.10
L	semibatch	4700	0.0658	0.763	20	14	10	498	320	1.4

Scheme 1. Dispersion ROMP Reaction of Norbornene (NB) in Dichloromethane/Ethanol Medium and in the Presence of a α-Norbornenyl Poly(ethylene oxide) Macromonomer (NB−PEO)



scribed the preparation of latex particles through dispersion copolymerization of PEO macromonomers, but they all resorted to free radical means. Although the mechanism of particle formation should be governed by essentially the same factors both in ring-opening metathesis dispersion polymerization and in free radical polymerization, one essential feature distinguishes the first type of chain addition process from the second one. ROMP implies that all polymeric chains are created within a short period and grow simultaneously, unlike the case of classical free radical polymerization. This means that graft copolymers prepared by ring-opening metathesis copolymerization should normally exhibit a same chemical composition whereas in those produced by free radical copolymerization the fluctuation in composition can be large. The simultaneous creation of chains by ROMP has another consequence mechanismwise: after the critical point, particles produced by ROMP should only grow by polymerization of the monomer occluded within themselves and not through the capture of newly created oligomers

Kinetics Results. Figures 1 and 2 show the respective conversions of both norbornene and **1** vs time. The rate of consumption of monomer is found to be considerably higher than that of the macromonomer. As illustrated graphically, norbornene was totally consumed after 5 min of reaction whereas only 10% of the PEO macromonomer reacted.

Such a difference in the rate of conversion of norbornene and **1** can be due to several reasons:[12]

- Poor accessibility to the terminal unsaturation carried by the macromonomer.
- Low concentration of macromonomer in the reaction medium compared to that of norbornene.
- Incompatibility between growing polymeric chains and the macromonomer.

In contrast to the case of norbornene, the complete conversion of **1** took a long time (Figure 2). This suggests a strong tendency to “blockiness” in such a copolymerization involving the PEO macromonomer. The polymeric structure formed is thus a gradient-type graft copolymer that contains very few PEO grafts at one end and includes progressively more and more to become an almost pure comb-type polymer at the other end.

Latex Characterization. The size of the particles formed was characterized using dynamic light scattering (DLS) and transmission electron microscopy (TEM) (Table 2).

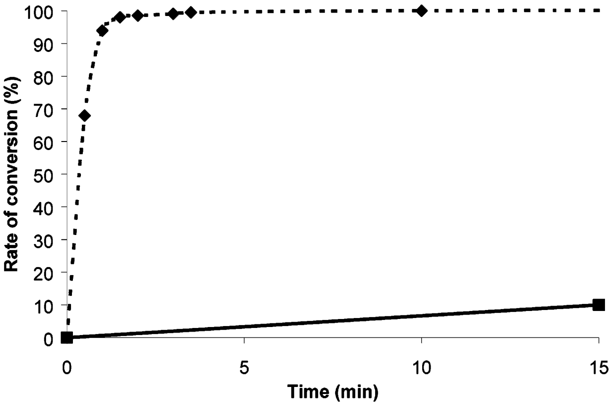


Figure 1. Conversion of norbornene (◆, NB) and PEO macromonomer (■, **1**) vs time for the dispersion ROMP of norbornene in CH_2Cl_2/EtOH (10/14 v/v) (A1, Table 2).

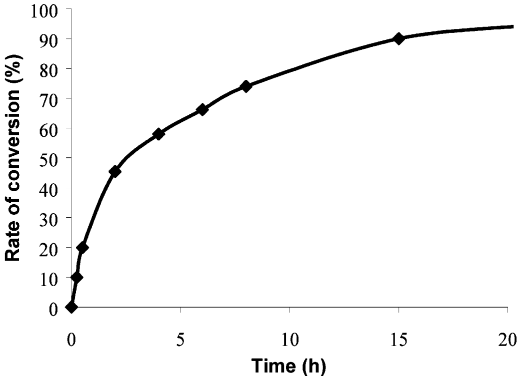


Figure 2. Conversion−time curve of PEO macromonomer (**1**) during the dispersion ROMP of norbornene in CH_2Cl_2/EtOH (10/14 v/v) (A1, Table 2).

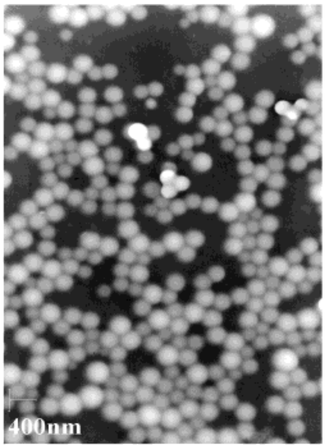


Figure 3. Transmission electron microscopy (TEM) micrograph of latex particles at $t = 18$ h (in the vicinity of 90% conversion of PEO macromonomer) (A1, Table 2).

Figure 3 shows a TEM micrograph of a PNB-*g*-PEO latex obtained after $t = 18$ h. These latex particles are monodisperse and mostly spherical and regular; they show no sign of coalescence. In contrast, TEM pictures of particles isolated at the early stage of polymerization show areas involving aggregates and irregular particles. This may be the sign of coalescence of particles due to a lack of stabilization by the slowly reacting macromonomer. Because of an insufficient contrast between the short PEO grafts and polynorbornene, the PEO surface layer could not be observed. The average particle size is on the order of 400 nm and one has to stress the good agreement between the size values obtained by microscopy (420 nm) and light scattering (440 nm) (entry A1, Table 2).

I.b. Influence of Experimental Conditions on the Particle Size and the Size Distribution. The size of the particles formed and their size distribution are known to depend on a number of parameters; some of them such as the macromonomer molar mass, its concentration, etc. were thus investigated in further detail. Data related to the particle size dependence are reported in Table 2, with values obtained by TEM and DLS.

Effect of the molar mass of PEO macromonomer 1. Two PEO macromonomers (**1**) of different molar mass were used: $\bar{M}_n = 4700$ g/mol (entry A1, Table 2); $\bar{M}_n = 7500$ g/mol (entry B, Table 2). As observed in free radical dispersion polymerization involving macromonomers as stabilizers,[13,14] macromonomers of larger molar mass also afford better stabilization in the present case which results in the formation of smaller particles. In experiment B, although fewer moles of macromonomers were used, stabilization was improved and smaller particles were eventually obtained. The size distribution also narrowed with increasing the chain length of **1**.

Effect of Macromonomer (1) Concentration. The initiator and monomer concentrations being kept constant, that of **1** was varied and its influence examined. As expected, the size of the particles decreases with increasing macromonomer concentration (entries A1, C, and D, Table 2). Higher concentrations of **1** produce a larger stabilizing surface area, causing the formation of smaller particles.

The influence of the macromonomer concentration on the size distribution is illustrated in a series of TEM pictures shown in Figure 4. Three different concentrations of stabilizer have been used (entries A1, C, and D, Table 2). With a low content of stabilizer (entry C), particles are mainly spherical. However, clear signs of coalescence can be discerned (Figure 4A). This can be ascribed to an insufficient amount of stabilizer on the particle surface. At a higher concentration (entry D), a broader particle size distribution is obtained which may be due to a secondary nucleation (Figure 4C). At the intermediate concentration (entry A1), neither renucleation nor significant signs of coalescence occurred (Figure 4_B).

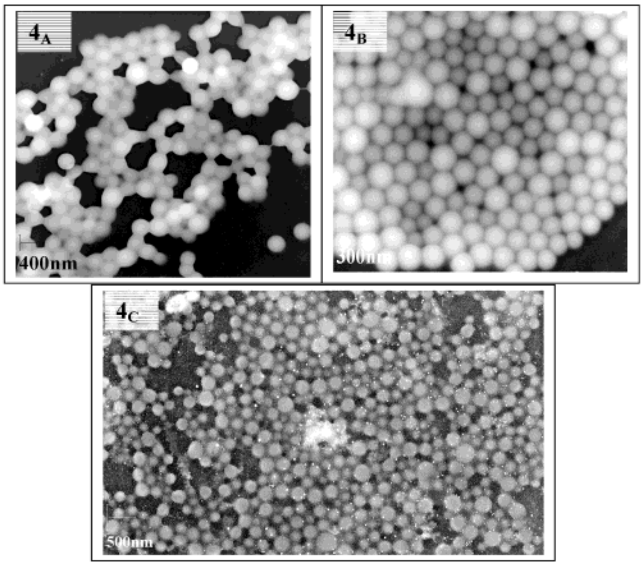


Figure 4. TEM pictures using different PEO macromonomer (**1**) concentrations: (A) $m(\mathbf{1}) = 0.329$ g (C, Table 2); (B) $m(\mathbf{1}) = 0.658$ g (A1, Table 2); (C) $m(\mathbf{1}) = 1.316$ g (D, Table 2).

Effect of Initiator Concentration. The initiator concentration is another parameter that was varied (20−40 mg). As reported in the literature for radical polymerization carried out in dispersed medium, an increase in the initiator concentration should normally lead to an increase of the particle size (entries A1 and E, Table 2). The following reasoning is generally proposed to account for the above observation: a higher initiator concentration (entry E) gives rise to a larger number of shorter polymeric chains. Such polymeric chains being more soluble in the medium, the nucleation step begins at a later stage of the polymerization. This results in a decrease of the number of particles which are thus of larger size. The same dependence of the particle size with the initiator concentration was also observed in our case with a tendency of the particle size distribution to narrow upon decreasing the initiator concentration.

Effect of Monomer Concentration. Upon decreasing the monomer concentration, smaller particles should normally form (entries A1 and F, Table 2). In our case, a 2-fold decrease in monomer concentration causes the latex particles to shrink to 240 nm, the distribution in size becoming broader. The monomer concentration is thus another crucial parameter for the control of the particle size.

Effect of Reaction Medium. The polarity of the reaction medium was also varied in order to determine its influence on the particle size. A more polar medium should normally induce an early nucleation of the particles and favors the formation of particles of smaller size (entry H, Table 2). As expected, the use of higher ethanol concentrations contributed to lower the critical

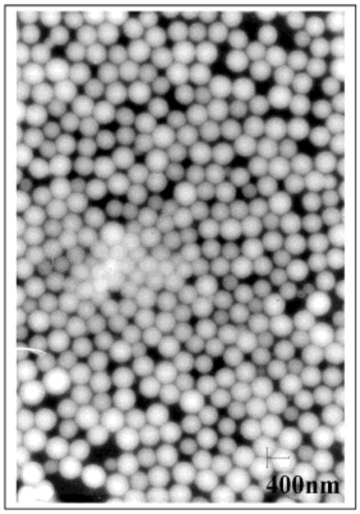


Figure 5. TEM photograph of latex particles synthesized by dispersion ROMP of norbornene in CH_2Cl_2/EtOH (14/10 v/v) using a less polar medium (entry G, Table 2). A rather narrow size distribution is obtained: $D_{n(TEM)} = 409$ nm; PDI = 1.02.

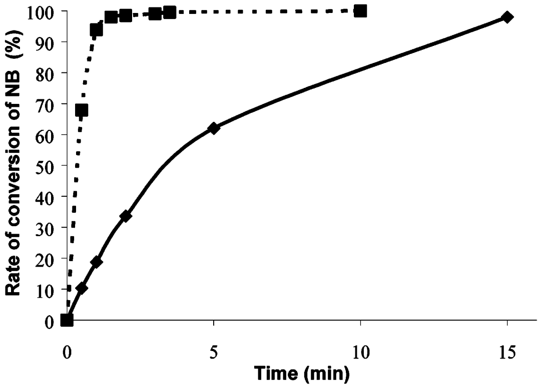


Figure 6. Norbornene conversion as a function of time for the dispersion ROMP of norbornene in CH_2Cl_2/EtOH (■, 10/14 v/v) and (◆, 14/10 v/v). Effect of the quality of the solvent mixture upon the polymerization kinetics (A1, G, Table 2).

chain length above which growing oligomers precipitate and smaller particles were thus generated. On the other hand, a less polar medium brought about the formation of rather monodisperse particles (entry G, Table 2), (TEM picture, Figure 5). The composition of the solvent mixture appears to be one of the most crucial parameters to obtain a narrow size distribution of particles.

The polarity of the medium also affects the kinetics of polymerization. Both norbornene and **1** are consumed slowly when the medium is less polar (Figures 6 and 7). Less than 40% of NB was converted in the dichloromethane-rich medium (entry G) whereas 95% of the same monomer was polymerized in the ethanol-rich medium (entry A1) after the same period of 2 min (Figure 6). These observations are consistent with those made by other teams[15] on classical free radical dispersion polymerization involving macromonomers: as soon as the first growing chains precipitate out of the medium and sterically stabilized particles are formed, which obviously occurred at very early conversion for the ethanol-rich system, the reaction loci are likely transferred from the solution to the polymer particles. This early compartimentalization of the reaction loci with a high concentration of NB within the particles explain why the latter monomer polymerizes much faster in the ethanol-rich system. In contrast, the composition of the reaction medium has only moderate impact on the rate of consumption of macromonomer (Figure 7). These results demonstrate the strong influence of the polarity of the medium on the critical point and the onset of the nucleation period, which in turn controls both the structure of the resulting graft copolymer and the colloidal characteristics of the latex particles formed (particle size and size distribution).

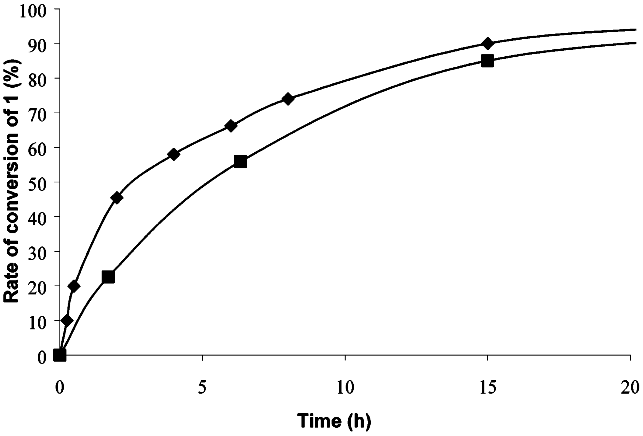


Figure 7. Conversion−time curve of PEO macromonomer (**1**) for the dispersion ROMP of norbornene in CH_2Cl_2/EtOH (◆, 10/14 v/v) and (■, 14/10 v/v). Effect of the quality of the solvent mixture upon the polymerization kinetics (A1 and G, Table 2).

Conclusions about the Particle Size and the Particle Size Distribution Dependence. As shown in the previous section, the particle size is influenced by most of the parameters investigated. Both the particle size and its size distribution indeed vary with the composition of the medium, the molar mass of the macromonomer, its concentration as well as those of the initiator and the monomer. Experimental conditions (more polar medium, low initiator concentration, etc.) that bring about an early nucleation obviously favor the formation of particles of smaller size and rather broad distributions. The latter feature (broadening of the distribution of sizes) indicates that the period of nucleation is not short enough or that premature particles continue to coalesce in the particle growth stage, two reasons that are not necessarily in contradiction with an early onset of nucleation. Indeed, the ROMP catalyst used in our experiments is a very reactive one that can be responsible for the formation of soluble polymeric species within the particles through intramolecular chain transfer and reshuffling reactions. Such soluble species may then nucleate upon further addition of monomer and in turn provoke a broadening of the particle size distribution. Conversely, a late onset of nucleation (less polar medium, high monomer and initiator concentrations) favored the formation of particles of larger size and narrower size distribution, which is indicative of a short period of nucleation. This is consistent with the previous observations and comments. However, a significant exception was observed when using a macromonomer (**1**) of larger size (entry B, Table 2) which helped to reduce not only the size of the particles formed but also their distribution. In the latter case only could small particle size be conjugated with a narrow distribution.

I.c. α-Norbornenyl Poly(styrene-*b*-ethylene oxide) Macromonomer (7) As Reactive Stabilizer. The type of macromonomer used to stabilize the par-

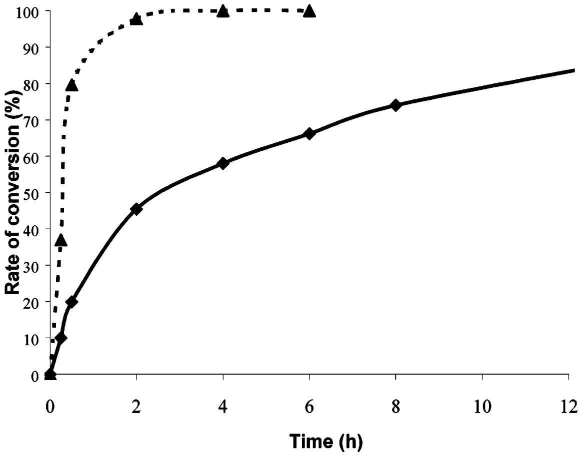


Figure 8. Conversion−time curve of reactive stabilizers for the dispersion polymerization of norbornene in CH_2Cl_2/EtOH (10/14 v/v) using **1** (◆) and **7** (▲) as stabilizers. Effect of the stabilizer's nature on the polymerization kinetics (A1 and A2, Table 2).

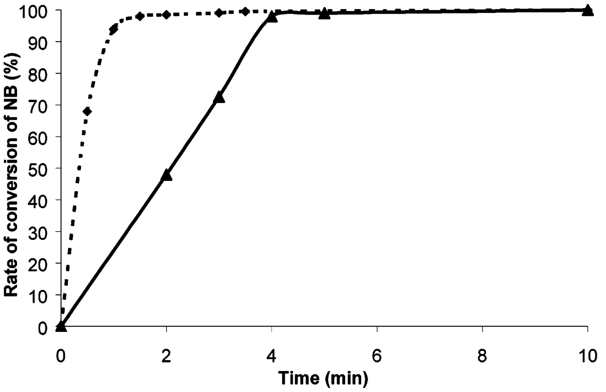


Figure 9. Polymerization kinetics of norbornene using different types of stabilizer: a PEO macromonomer (◆, **1**) and an amphiphilic PEO macromonomer (▲, **7**). Effect of the stabilizer's nature on the kinetics of polymerization (A1 and A2, Table 2).

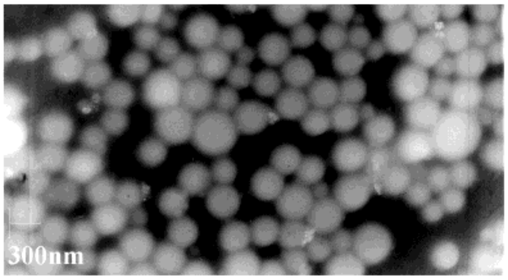


Figure 10. TEM micrograph of polynorbornene-based particles prepared by dispersion ROMP using an amphiphilic PEO macromonomer (**7**): $D_{n(TEM)} = 318$ nm; PDI = 1.10 (A2, Table 2).

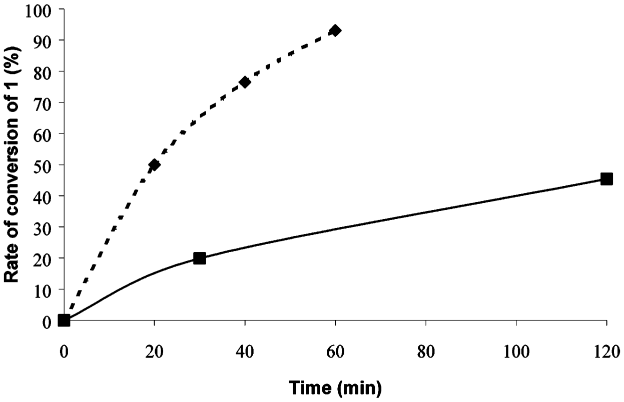


Figure 11. Conversion−time curve of PEO macromonomer (**1**) for the dispersion ROMP of norbornene in CH_2Cl_2/EtOH (10/14 v/v) by varying the monomer addition policy: (◆, semibatch process; ■, batch process). Effect of the batchwise upon the polymerization kinetics (A1 and I, Table 3).

ticles formed was also varied so as to investigate the relation between the amphiphilic character of macromonomers on one hand and the kinetics of polymerization and the characteristics of the latex particles on the other. The behavior of hydrophilic macromonomers compared to that of their amphiphilic analogues remains indeed a disputed issue with opposite conclusions being reported in the literature of free radical dispersion copolymerization.[16] In this work, NB−PS-*b*-PEO macromonomers including a PEO block of same size as that of **1** and a short PS block ($\bar{M}_n = 1700$ g/mol) were introduced in the reaction medium along with the monomer and the initiator. It must be stressed that such amphiphilic macromonomers do not self-aggregate in such a dichloromethane/ethanol medium as checked by DLS analysis, surface tension vs concentration measurements, and TEM observations.

Kinetics Results. Figures 8 and 9 show the respective conversions of **7** and norbornene as a function of time. Compared to the dispersion polymerization of NB carried out in the presence of **1**, the rate of consumption of the cycloolefin with **7** as reactive stabilizer is significantly slower: the conversion reaches 40% after 2 min of polymerization in contrast to 95% in the presence of **1**. In contrast, **7** is consumed much faster than **1**: about 80% of **7** macromonomer is incorporated in the particle after 2 h of reaction whereas only 45% of **1** was polymerized after the same period. The difference in rate of conversion between **1** and **7** can readily be explained by the amphiphilic structure. The polystyrene block offers the hydrophobicity necessary for the stabilizer to anchor at the particle surface. Consequently, such macromonomers can provide a better stabilization because of a faster incorporation into the growing chains.

Latex Characterization. Figure 10 shows a TEM micrograph of latex particles stabilized by **7**. Compared to the particles obtained with **1**, the latex size decreases when **7** is the reactive stabilizer (entry A2, Table 2). Owing to the affinity of **7** for the particle surface, latexes get stabilized at an early stage of polymerization, which leads to the formation of smaller size particles. This experiment again showed that the presence of an end-standing unsaturation allowed the emulsifier to efficiently function as a stabilizer.

The distribution in size is however broader (PDI = 1.10) than with **1** as reactive stabilizer. A longer period of nucleation is likely responsible for the broadening of the distribution observed.

II. Semibatch Process. In another series of experiments designed at examining the impact of the rate of addition of NB on the particles formed, the cycloolefin was added over a period of 1 h to the reaction medium containing the Grubbs initiator and **1**. It must be stressed that the concentrations of all reactants were chosen identical to those of the batch process. The NB incorporation rate being slowed by the continuous addition, one can therefore expect the graft copolymer formed to exhibit a different structure and different colloidal properties.

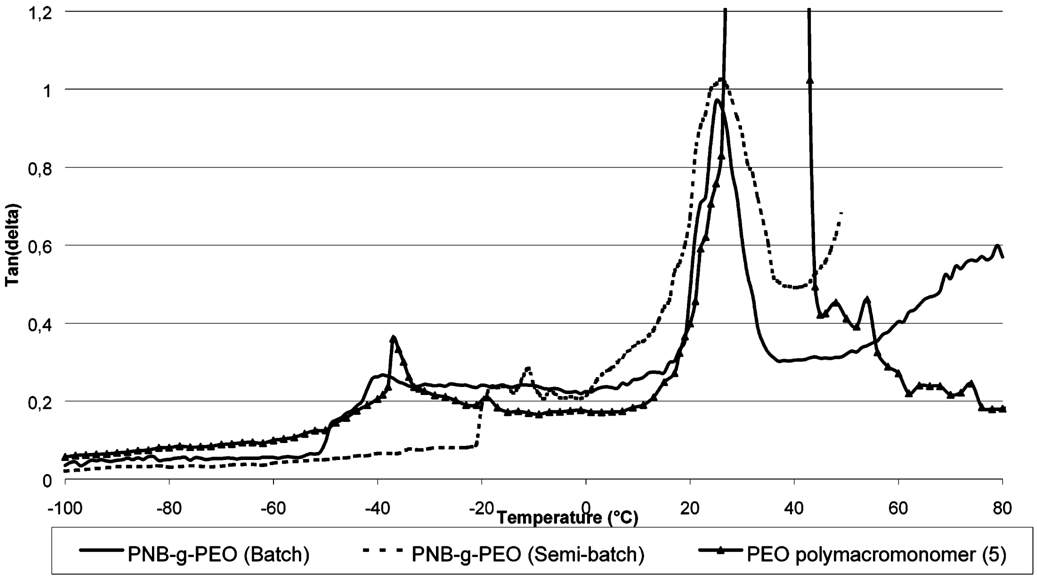


Figure 12. Dynamic mechanical spectra showing the variation of tangent delta with temperature: for copolymers prepared by dispersion ROMP of norbornene by the use of batch process (−) and semibatch process (···); for PEO polymacromonomer (▲, **5**).

Kinetics Results. The experimental conversion curve of PEO macromonomer (**1**) is given in Figure 11. As shown in this plot, the macromonomer consumption was considerably affected by changing the addition rate of NB. The incorporation rate of macromonomer was significantly increased when NB was continuously introduced into the reaction medium. Complete conversion was achieved after only 1 h of reaction instead of several hours for the batch process. Under such conditions, an instantaneous consumption of norbornene is achieved as soon as monomer is introduced in the reaction vessel. We inferred from these results that a random graft copolymer of relatively uniform composition was actually obtained under these semibatch conditions. In contrast, the batch process afforded graft copolymers with a blocky structure.

Dynamic Mechanical Analysis (DMA). The difference in the distribution of grafts between the two types of copolymers has been confirmed by DMA analysis. The dynamic mechanical spectra of films formed from the latex produced by batch and semibatch processes are shown in Figure 12. For comparison, the DMA spectrum of the PEO polymacromonomer (**5**) has also been reported.

Whatever the rate of addition of NB, two distinct glass transition temperatures can be observed corresponding to the two polymer phases present: polynorbornene (at $T = 25$ °C) and PEO (in the range −40 to −20 °C).

•Batch and semibatch copolymers show an identical peak at $T = 25$ °C, which corresponds to the glass transition of polynorbornene. Regardless of the copolymer composition distribution, the position and the shape of the peak remain unchanged.

•In contrast, the glass transition temperature corresponding to the PEO grafts reveals differences with the copolymer considered. In the copolymer obtained by the batch process, the glass transition peak for PEO grafts is found at $T = -37$ °C against −21 °C in the semibatch copolymers. Obviously, the PEO glass transition temperature is firmly affected by the copolymer composition distribution. A similar value of T_g (−37 °C) was measured for the PEO-based polymacromonomer (**5**), confirming the "blocky" structure of the graft copolymer synthesized using the batch process.

Latex Characterization. The semibatch strategy gives rise to significant changes in the particle size as well (Table 3). The particles are spherical but significantly smaller (from 155 to 300 nm) than those produced by the batch process.

The particle size slightly decreases with increasing the polarity of the reaction medium (entry J, Table 3), which is in agreement with previous observations. In addition, this semibatch process allowed to use much less reactive stabilizer, a 4-fold or 10-fold decrease in the amount of PEO macromonomer (**1**) resulting in a marginal increase of the particle size (entries K and L, Table 3). In any case, the particle size distribution was rather broad due to a possible secondary nucleation and particle coalescence. On the other hand, this method exhibits the serious disadvantage that randomly distributed PEO grafts increase the formation of soluble copolymers, which represents a waste of product.

III. Dispersion Polymerization of NB in the Presence of Unreactive Stabilizers. Unlike particles obtained in the presence of a macromonomer, the use of an unreactive stabilizer in the dispersion polymerization of NB should result in latex of pure polynorbornene. The question that was addressed through these experiments is whether pure PNB particles can be formed in the presence of unreactive stabilizing agents.

III.a. Poly(ethylene oxide) Homopolymer (2) As Stabilizer. Under identical experimental conditions, a PEO homopolymer (**2**) of same molar mass as that of the macromonomer **1** and possessing an unreactive chain end was thus added to the reactive medium. It appears that the PNB chains formed precipitates out of solution in the early stage of polymerization. The incompatibility of **2** for polynorbornene prevented its significant adsorption onto the forming particle surface to stabilize them.

This experiment showed the important role played by the unsaturation of the macromonomer in the stabilization process, whose copolymerization with the growing chains provided enough steric repulsion to prevent the coalescence of particles.

III.b. Unreactive Amphiphilic Copolymers (3, 4, 5, 6) As Stabilizers. Several other unreactive polymeric structures based on PEO (Table 1) were tried as

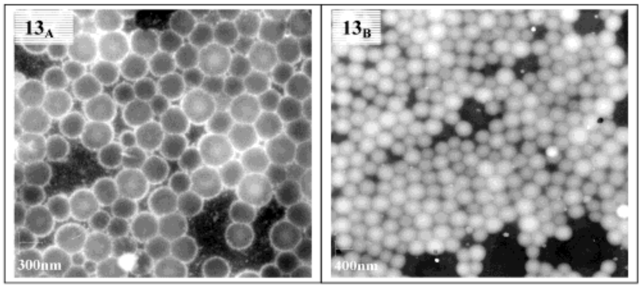


Figure 13. (A) TEM picture representing a preformed seed dispersion: $D_{n(TEM)} = 365$ nm. (B) Effects of a second shot of monomer and initiator upon particle size: $D_{n(TEM)} = 437$ nm.

stabilizers, but none of them could prevent the PNB formed from precipitating.

Amphiphilic block copolymers, whether they contain a PS block (**3**) or a hydrocarbon segment (**4**) failed to adsorb sufficiently on the forming PNB particles, likely because of a too low affinity of the hydrophobic part for PNB. Precipitation of the PNB was indeed observed at the very early stages of reaction.

Unexpectedly, a graft copolymer PNB-*g*-PEO (**6**) and a polymacromonomer (**5**) obtained from the homopolymerization of **1** were also found to be inefficient at stabilizing PNB particles.

In the case of **5**, it appears that the benefits provided by the polynorbornene backbone were significantly counterbalanced by its multibranched structure and high solubility in the reaction medium. Likewise, if **6** could not prevent PNB from precipitating this is certainly due to its high content in PEO grafts: as our initial aim was to investigate the dispersion polymerization, we had no other option but to use a PEO-rich graft copolymer in order to start with a clear homogeneous medium. In other words, such preformed soluble copolymers (**6**) exhibit a composition that is different from the polymer formed "in situ" by the copolymerization of **1** with the cycloolefin. Another factor that played against such nonreactive stabilizing agents is the fast NB conversion: the critical chain length is reached very rapidly whereas most stabilizers have not yet been adsorbed.

At this stage, only PEO macromonomers that were fitted with a polymerizable norbornenyl entity proved to be well-suited to stabilize latex particles.

IV. Seeded Dispersion Polymerization. In our attempt to generate particles of PNB, an alternative approach consisted in using preformed seeds of PNB-*g*-PEO-based latex. This seed ($D_n = 365$ nm) was synthesized by ROMP dispersion of norbornene in the presence of a PEO macromonomer (**1**) as previously described. Subsenquently, a second aliquot of monomer and initiator were introduced so as to grow pure polynorbornene chains. Surprisingly, these newly formed polymers did not nucleate to give rise to a new crop of pure PNB particles; they were captured by the seed particles present in the continuous medium and therefore contributed to the growth of the latter. As evidenced by TEM (Figure 13), the initial seed particles (365 nm) could then grow up to 437 nm through capture and growth of PNB chains but also through coalescence. The number of particles, indeed decreased (from 2.2×10^{12} to 1.3×10^{12} particles/mL of latex) significantly.

Conclusion

In this work, two types of polynorbornene-based particles have been obtained via dispersion ring-opening metathesis polymerization of norbornene. In the first instance, latex of PNB-*g*-PEO copolymers have been generated by carrying out dispersion polymerizations in the presence of a α-norbornenyl PEO macromonomer (**1**). Such reactive stabilizers whether they contain a hydrophobic block (NB−PS−PEO, **7**) or not (**1**) proved to be well-suited to stabilize latex particles. Several parameters including the polarity of the medium, the concentrations of reactants, etc. and also the rate of addition of NB were investigated with a view of determining their influence on the colloidal properties and the type of graft copolymers produced. Latex particles could be obtained in the range 300−400 nm with a rather narrow distribution using appropriate macromonomers and medium compositions. As to the structure of the graft copolymer formed, the batch process was found to favor the formation of "blocky" graft copolymers whereas the semibatch essentially afforded random graft copolymers. The last part of this study was devoted to the synthesis of pure PNB latexes in the presence of unreactive stabilizers or PNB-*g*-PEO seeds. This seeded dispersion polymerization was actually the only route affording stable PNB latex particles.

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