Latex Particles by Miniemulsion Ring-Opening Metathesis Polymerization

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ABSTRACT: Polynorbornene latexes were prepared by ring-opening metathesis polymerization of norbornene (NB) in water carried out in miniemulsion. The ability of both lipophilic or hydrophilic initiators to polymerize NB under miniemulsion conditions has been investigated. With an oil-soluble initiator ($(Cy_3P)_2Cl_2Ru{=}CHPh$) the miniemulsion polymerization of NB resulted in the formation of large and poorly stabilized particles that eventually coagulated. On the contrary, with a water-soluble initiator based on $RuCl_3$ and an alcohol stable particles could be obtained as a result of the miniemulsion polymerization of NB. For each miniemulsion polymerization the role played by ionic and steric stabilizers such as sodium dodecyl sulfate and poly(styrene-*b*-ethylene oxide), respectively, on both the course of polymerization in miniemulsion and the particle stabilization has been investigated in detail.

Introduction

The current trend for a sustainable and green chemistry emphasizing in particular the use of environment-friendly solvents makes ring-opening metathesis polymerization (ROMP) in aqueous medium an attractive option as well as interesting scientific challenge.[1] The very first attempts to polymerize norbornene (NB) in water under emulsion conditions were however reported as early as 1965 by Rinehart[2,3] and Michelotti,[4] who used hydrates of ruthenium, iridium, and osmium chlorides as catalysts in the presence of a reducing agent such as aliphatic alcohols, sodium borohydride, or stannous salts. The emulsions obtained were stabilized by an anionic or a steric surfactant—sodium dodecylbenzenesulfonate (SDBS) or (poly(ethylene oxide)-*b*-poly(propylene oxide))—but little detail was given about the colloidal characteristics (size of particles, polydispersity, etc.). 7-Oxanorbornene is another monomer that subjected to ROMP in water by Booth et al.,[5] who used poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer and ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$) as stabilizer and catalyst, respectively. The particle sizes were found to range from 18 to 164 nm. More recently, Wache[6] reported the synthesis in water of SDBS-stabilized PNB latexes with an unusually high cis content, using water-soluble bis(allyl)ruthenium(IV) complexes. With the availability of well-defined ruthenium-based alkylidenes[7,8] exhibiting both high reactivity and tolerance of polar media significant advances could be made in the applicability of ROMP in dispersed aqueous media.[9,10] For instance, Claverie et al.[11] used the water-soluble complex $RuCl_2(PCy_2(C_5H_{10}NMe_2Cl))_2(CHPh)$ and anionic surfactants (sodium dodecyl sulfate (SDS) or sodium decyldiphenyloxide disulfonate (Dowfax)) to obtain stable PNB nanoparticles with sizes varying from 50 to 100 nm by emulsion polymerization. To polymerize less strained cyloolefins such cyclooctadiene (COD) and cyclooctene (COE) the same authors preferred the more active initiator, $RuCl_2(PCy_3)_2CHPh$ (**1**). The latter hydrophobic complex was dispersed under the form of toluene miniemulsion droplets stabilized with SDS and latexes of high molar mass polymers could be obtained in this way. However, the nanoparticles obtained in the size range from 250 to 650 nm were prone to flocculation.

In a recent addition to this field,[12−18] we showed that latexes of PNB and polybutadiene can easily be synthesized in alcoholic or aqueous media by dispersion or suspension ROMP with the presence of a norbornenyl poly(ethylene oxide) macromonomer added to stabilize the particles formed. The results obtained prompted us to extend this study to the synthesis of PNB particles by means of a miniemulsion process.

In this paper, miniemulsion polymerization of NB in water has been investigated in detail. Three different approaches have been contemplated. First, the polymerization of NB miniemulsion was carried out in the presence of an oil-soluble initiator (**1**). In the latter case, **1** was added to a miniemulsion of NB under different conditions: organic solution, aqueous emulsion, or aqueous miniemulsion. In a second approach, **1** solubilized in toluene was dispersed in water by miniemulsification in the presence of a surfactant, and then monomer was added to this miniemulsion. Finally, the third approach consisted of using a water-soluble initiator ($RuCl_3 \cdot xH_2O$ (**2**) in alcohol) to initiate the polymerization of NB in miniemulsion.

Experimental Section

Materials. All reagents were purified according to standard procedures and stored under an inert atmosphere. Norbornene (NB) was stirred over sodium at 70 °C for 7 h and subsequently distilled. ROMP reactions were carried out under an inert atmosphere in a 100 mL glass jacketed reactor fitted with a mechanical stirrer, an argon inlet, and a sampling valve. Poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) stabilizer was prepared according standard procedure ($\bar{M}_{n,PS,SEC} = 1600$ g/mol; $\bar{M}_{n,PEO,NMR} = 14\,000$ g/mol, PDI $= 1.12$).

Size Exclusion Chromatography (SEC). Molar masses and molar mass distributions were determined by SEC. The SEC equipment consisted of a TOSOHAAS TSK gel column equipped with JASCO HPLC pump type 880-PV connected to a Varian refractive index detector and a JASCO 875 UV/vis absorption detector, THF being the mobile phase. Calibration was carried out with polystyrene standards. To obtain actual

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Table 1. Miniemulsion ROMP of NB with $(PCy_3)_2Cl_2Ru{=}CHPh$[a]

expt	surfactant	V_{water} (mL)		V_{toluene} (mL)		T (°C)
P1	SDS	50		1		20
P2	PS-*b*-PEO					
S1	SDS	50		0.7	0.3	20
S2	PS-*b*-PEO					
S3	SDS	50		0.7	0.3	5
S4	PS-*b*-PEO					
S5	SDS	50		0.7	0.3	80
S6	PS-*b*-PEO					
S7	SDS	50		0.7	0.3	20
S8	PS-*b*-PEO					
E1	SDS	40	10	0.7	0.3	20
E2	PS-*b*-PEO					
M1	SDS	40	10	0.7	0.3	20
M2	PS-*b*-PEO					

[a] C_{NB} = 35 g/L; m_{HD}/m_{NB} = 0.04; [NB]/[cat.] = 2119. A conversion of 100% of NB was found in all experiments.

molar masses, the values given have to be divided by a factor of 2.1, as demonstrated in previous paper.[19]

Droplet and Particle Size. Droplet and particles sizes were obtained from dynamic light scattering (DLS) with a MALVERN zetazizer 3000 equipped with a He−Ne laser. The shelf life stability of the miniemulsion was studied by measurement of the evolution of the droplet size over time. Samples for the monomer-droplet size measurements were prepared by dilution (about 100 times) of the miniemulsion to minimize multiple scatterings caused by high concentration. The dilution water was obtained by separating the aqueous phase of the miniemulsion by ultracentrifugation. Standard deviations were calculated for each miniemulsion according to the literature.[20]

Gas Chromatography (GC). The rate of conversion of norbornene was determined by gas chromatography. The apparatus consisted of a FID dectector (Varian 33650) coupled with hydrophobic capillary column (BP1-30 m). Toluene was used as internal standard. T_{inj} = 250 °C, T_{detec} = 280 °C, T_{init} = 50 °C (10 °C/min); Vector gas: N_2.

Miniemulsion Preparation and Polymerization. All reactions, whose recipes are given in the next section, were carried out according to the following procedures.

Polymerization of NB Miniemulsion with 1 (Table 1). The surfactant ([SDS] = 3 g/L; [PS-*b*-PEO] = 10 g/L) was dissolved in 50 mL of distilled−deionized (DDI) water. In a separate container, hexadecane (HD) (4 wt % to the monomer) and NB ([NB] = 35 g/L) were dissolved in a desired amount of toluene (0.7−1 mL). The oily and aqueous solutions were mixed under vigorous mechanical agitation for 1 h. This step was followed by further mixing under magnetic agitation in an ultrasonic homogenizer equipped with a cylindrical probe (Sonic W750) at 50% of the power for 2 min. During the sonication step, the vessel containing the miniemulsion was immersed in an ice bath to prevent it from heating. To carry out the polymerization, the miniemulsion was transferred under nitrogen into the polymerization reactor, equipped with mechanical stirrer and water condenser. Before the reaction started, the reactor was purged with nitrogen for 1 h at the desired temperature. In an argon-filled drybox, the Grubbs initiator (**1**) (7 mg) was dissolved in toluene (0.3 mL) before its addition to the miniemulsion in order to trigger the polymerization.

Polymerization of NB from Miniemulsion of 1 (Table 2). In a typical recipe, surfactant ([SDS] = 3 g/L, [PS-*b*-PEO] = 10 g/L) was dissolved in 50 mL of DDI water and then purged under nitrogen for 1 h. In an argon-filled drybox, the Grubbs catalyst (**1**) (7 mg) was dissolved in a mixture of toluene (2 mL) and HD (4 wt % to the toluene). This purple solution was then added outside the drybox to the stabilizer water solution and stirred over 1 h. The miniemulsion was prepared by sonicating the mixture for 2 min at 50% amplitude (Sonic sonifier W750). During the sonication step, the vessel containing the miniemulsion was immersed in an ice bath to prevent it from heating. The miniemulsion was then transferred under nitrogen into the polymerization reactor heated at the desired temperature. After 15 min of stirring (600 rpm), preheated monomer solubilized in toluene (2 mL) was added dropwise to the miniemulsion. The initially purple miniemulsion became light gray.

Polymerization of NB Miniemulsion with 2 (Table 3). Procedure 1: NB miniemulsion was prepared according to the previously described procedure. The catalyst solution was prepared according to the work published by Basset et al.[21] **2** was dissolved in alcohol ([alcohol] = 30 g/L) and heated at 60 °C for 30 min under nitrogen before its addition to the NB miniemulsion.

Polymerization of NB miniemulsion with 2 (Table 3, Experiment M11). Procedure 2: A similar procedure was carried out except that 1.5 equiv of NB was added to the catalyst solution before heating.

Results and Discussion

1. Miniemulsion Polymerization of NB with Lipophilic Complex 1.

A miniemulsion is a kinetically stable emulsion whose droplet sizes range from 50 to 500 nm. To prevent any colloidal degradation during the polymerization by molecular diffusion (Ostwald ripening), a lipophilic agent—usually hexadecane—is added to the oil phase. In ideal systems, droplets are stable during the polymerization step. The resulting polymer particles are thus the perfect one-to-one copy of the monomer droplets in size and size distribution. In a typical radical miniemulsion polymerization monomer and initiator are mixed together prior to the emulsification step (sonication, microfluidization). Owing to the high reactivity of **1** with NB even at low temperature, a similar procedure could not be applied in our case, and others procedures had to be contemplated. The first procedure consisted in introducing **1** into a miniemulsion of NB. In the second procedure, NB was added to a miniemulsion of **1**: in the latter case the term of polymerization in miniemulsion may not be appropriate because polymerization occurred in a miniemulsion of initiator and not in the monomer one. In both cases, PS-*b*-PEO and SDS were used as stabilizer.

1.1. Polymerization of NB Miniemulsions with 1. Miniemulsion Stability. The stability of the monomer miniemulsion is an important factor because it directly affects the miniemulsion polymerization process and hence particle size distribution. The miniemulsion of monomer must be in particular stable during the time elapsed between its preparation and the onset of the polymerization and throughout all of it.

The stability of NB miniemulsions against both molecular diffusion and coalescence was ensured by the presence of a lipophilic agent (HD) and SDS or PS-*b*-PEO stabilizers and checked by dynamic light scattering (DLS) (Figure 1). As expected, the droplet size was smaller with ionic stabilization (SDS) (75 nm) than with steric stabilization (PS-*b*-PEO) (220 nm). This result can be attributed to the difference in the size of the two stabilizers (molecule compared to a polymer) and combined to the need of a more dense surfactant packing with steric stabilizer to be as efficient as the ionic one.[22] For the same reasons, the particle size distribution (PSD) was broader for nonionic latexes compared to ionic homologues:[23] the standard deviation was found to be lower than 32% for the ionic stabilization and below 36% for steric one. Droplet size was found to be constant for 20 h, after which a slow increase could be detected.

Table 2. ROMP of NB from Catalyst 1 Miniemulsion[a]

expt	surfactant	rate of NB addition (mL/h)	solvent for NB (mL)	T (°C)	coagulation (%)	D_g (nm)	D_p (nm)
P1	SDS	10	toluene:**2**	10	93	94	184
P2	PS-*b*-PEO				91	231	291
P3	SDS	10	toluene:**2**	20	86	98	198
P4	PS-*b*-PEO				82	236	324
P5	SDS	10	toluene:**2**	60	71	95	217
P6	PS-*b*-PEO				67	240	387
P7	SDS	10	toluene:**2**	80	59	100	232
P8	PS-*b*-PEO				54	252	419
P9	SDS	5	toluene:**2**	80	40	96	298
P10	PS-*b*-PEO				40	232	475
P11	SDS	1	toluene:**2**	80	28	91	346
P12	PS-*b*-PEO				26	236	519
P13	SDS	0.5	toluene:**2**	80	25	98	363
P14	PS-*b*-PEO				25	235	535
P15	SDS	1	tetrahydrofuran:**2**	60	65	93	340
P16	PS-*b*-PEO				68	239	396
P17	SDS	1	tetrahydrofuran:**2**	80	45	98	450
P18	PS-*b*-PEO				43	241	478

[a] $C_{NB} = 35$ g/L; [NB]/[cat.] = 2119. A conversion of 98% of NB was found in all experiments.

Table 3. Miniemulsion ROMP of NB with Hydrophilic Initiator Based on $RuCl_3 \cdot xH_2O$/Alcohol (2)[a]

expt	surfactant	procedure	alcohol	$C_{alcohol}$ (g/L)	[NB]/[cat.]	conv (%)	D_g (nm)	D_p (nm)
M1	SDS	1	1-butanol	30	110	70	74	216
M2	PS-*b*-PEO	1				68	216	223
M3	SDS	1	1-butanol	80	110	75	75	512
M4	PS-*b*-PEO	1				82	219	
M5	SDS	1	none		110	16	78	122
M6	PS-*b*-PEO	1				10	218	219
M7	SDS	1	benzyl alcohol	30	110	90	76	302
M8	PS-*b*-PEO	1				98	232	
M9	SDS	1	1-butanol	30	55	76	76	223
M10	PS-*b*-PEO	1				74	216	222
M11	SDS	2	1-butanol	30	110	70	76	218

[a] $C_{NB} = 30$ g/L, $T = 60$ °C.

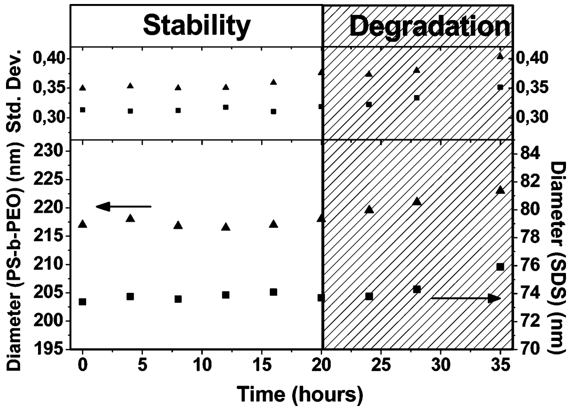


Figure 1. Stability of NB miniemulsion: diameter of NB droplets and standard deviation of droplet size distribution against time: (■) droplets stabilized with SDS; (▲) droplets stabilized with PS-*b*-PEO.

Miniemulsion Polymerization. Table 1 shows the conditions used to carried out the polymerization of NB in miniemulsion with **1** as initiator. The latter was added to the preformed stable NB miniemulsion in different ways: directly in the form of powder (experiments P1−2), in solution in toluene (S1−8), and dispersed in aqueous emulsion (E1−2) or aqueous miniemulsion (M1−2). In each case consumption of NB was close to the unity. Unfortunately, all these trials resulted in a rapid and complete coagulation of the medium after 5 min of reaction whatever the stabilizer used (SDS or PS-*b*-PEO). No real improvement was observed upon varying parameters such as the temperature or the catalyst concentration.

These results can be accounted for the strong lipophilicity of **1**. Once introduced in the reaction medium, the initiator solution forms large and poorly stabilized separate droplets that disrupt the equilibrium of the miniemulsion. The polymerization mainly occurs in these new initiator droplets through collisions and coalescence, a process that afforded ill-stabilized polymer particles which rapidly coagulated.

A second approach was then tried based on the used of miniemulsion of **1** to which a solution of NB was added.

1.2. Polymerization of NB Using Miniemulsions of 1. The strong lipophilicity of **1** was thus exploited to prepare catalyst miniemulsion whose stability was checked by DLS (Figure 2). Average droplet sizes of 95 and 240 nm were found with SDS and PS-*b*-PEO stabilizers, respectively, with a classical standard deviations (<35%), attesting to the good stability of the formed miniemulsions for at least 25 h.

NB was then slowly added to the reaction medium from a microfeeder by dripping at a constant rate to allow the diffusion of the monomer to the initiator droplets through the water medium. The effect of the rate of NB addition, the nature of the solvent, the impact of the temperature, and the choice of the stabilizer on the size and coagulation of the latexes have been studied in detail. The data are shown in Table 2. Particles with sizes ranging from 180 to 535 nm were generated with complete conversion of NB for both types of stabilization (ionic and steric). The final particle size was always larger than that of the initiator droplets, attesting to the progressive diffusion of NB into the

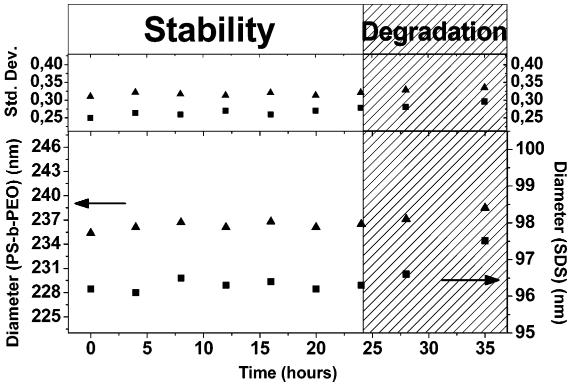


Figure 2. Stability of catalyst miniemulsion: diameters of catalyst droplets and standard deviation of droplet size distribution against time: (■) droplets stabilized with SDS; (▲) droplets stabilized with PS-*b*-PEO.

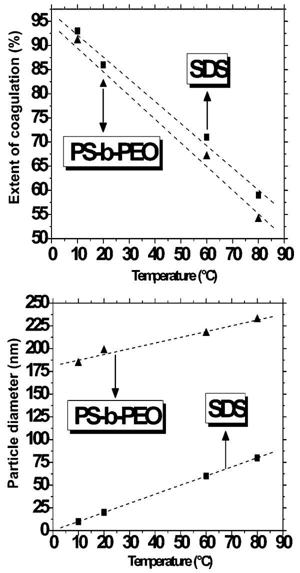


Figure 3. Plot of the extent of coagulation and particle diameter against temperature for NB polymerization with **1**: (■) SDS stabilization; (▲) PS-*b*-PEO stabilization.

latter. However, for each polymerization a large amount of coagulum could not be avoided. One explanation might be the partial diffusion of **1** through aqueous phase, but this hypothesis appears improbable due to the highly hydrophobic character of **1**. Another reason might be the strong hydrophobic character of the monomer itself which prevented its diffusion through aqueous phase and favored its aggregation in large droplets that destabilized the entire emulsion by collision/coalescence.

To check the pertinence of this hypothesis, the impact of both temperature and the rate of NB addition on the extent of coagulation and on the final particle size were examined. It clearly appears that the coagulum content decreases from 93% to 25% with an increase of the temperature and a decrease of the rate of addition of NB.

Figure 3 shows the direct dependence of the temperature on the amount of coagulum observed. With an increase of the temperature (experiments P1–P8, Table 2), NB became liquid, and its mobility/diffusion through water from its own droplets to particles was improved, which resulted in an increase of the final particle size.

Figure 4 shows the impact of the rate of NB addition on the amount of coagulum and on the final particle size.

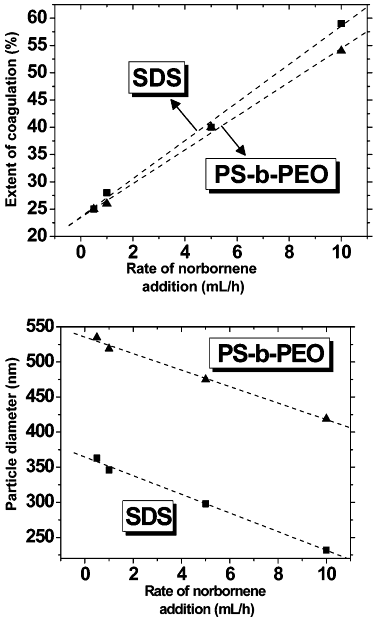


Figure 4. Plot of the extent of coagulation and particle diameter against the rate of NB addition: (■) SDS stabilization; (▲) PS-*b*-PEO stabilization.

When decreasing the rate of addition of NB (experiments P7–P14), the instantaneous NB concentration followed the same trend and also the amount of free NB diffusing to initiator particles. As a consequence, the amount of coagulum decreased and the final particle size increased.

As shown in Table 2, the choice of ionic or steric stabilizers is without significant effect on the particle stability. Indeed, if the particle size grows throughout polymerization due to the diffusion of NB, the amount of coagulum remains approximately the same with SDS and PS-*b*-PEO stabilizer.

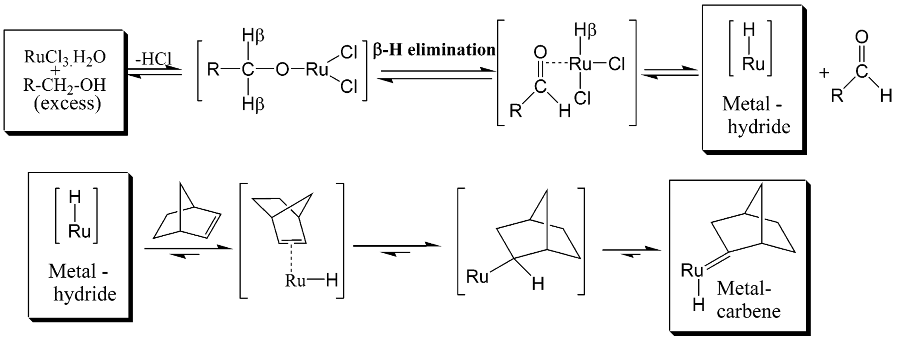
In experiments P15–P18, NB was dissolved in tetrahydrofuran (THF). This change of solvent had a drastic effect and resulted in an increase of the extent of coagulation. The solubility of THF in water might have favored the formation of large insoluble NB droplets that have destabilized the entire emulsion by the collision/coalescence process.

2. Miniemulsion ROMP of NB with 2 as Initiator. **2**, a water-soluble catalyst, is widely used to initiate ROMP of norbornene, oxanorbornene, and their derivatives in aqueous and alcoholic solvents. We explored here the possibility of using this industrial catalyst for the miniemulsion ROMP of NB. Several studies have been carried out to elucidate the structure[1] of active species involved in this reaction (metal hydride, metal–oxo, water-assisted mechanism, etc.). The metal carbene structure, reported by Basset et al.,[21] involving the formation of an intermediate metal hydride complex, is the most accepted one (Scheme 1).

Table 3 shows the results of miniemulsion ROMP of NB initiated with ruthenium trichloride, **2**. Various parameters such as the type of surfactant and the nature and concentration of catalyst were varied to check their impact on the conversion rate and particle size.

Particles of polynorbornene exhibiting a size ranging from 220 to 520 nm and a good stability were successfully generated without formation of any coagulum. Depending on the experimental conditions used conver-

Scheme 1. Metal−Hydride Mechanism



sion of NB ranged from 10% to 90% after 15 h of reaction.

Experiments carried out in the presence of PS-*b*-PEO steric stabilizers resulted in stable latex particles exhibiting about the same size as that of the initial NB droplets. On the contrary, the use of SDS brought about a large variation in the size of the monomer droplets and that of particles. Steric stabilizers appeared thus more efficient than ionic ones to prevent the degradation of the miniemulsion formed. To determine the origin of this degradation, the size of the droplet/particle radius (r) vs time was measured before and after addition of the alcoholic catalyst solution. If coalescence is the driving force, r^2 should increase linearly with time whereas linear r^3 vs time variation would be indicative of a degradation by Ostwald ripening.[24] As shown in Figure 1, the SDS-based NB miniemulsion is perfectly stable over at least 12 h. However, after addition of the catalyst solution the variation of r^2 and r^3 with the reaction time indicates that the miniemulsion undergoes a phenomenon of coalescence (Figure 5, experiment M1). It thus appears that the miniemulsion is slightly destabilized upon contact with 1-butanol. An explanation might be that the latter alcohol induces the desorption of ionic surfactant molecules from the interface to the solution resulting in the breaking of the interfacial film. As expected, an increase of the butanol concentration from 30 g/L (experiment M1, Table 3) to 80 g/L (experiment M3, Table 3) speeds up the coalescence process.

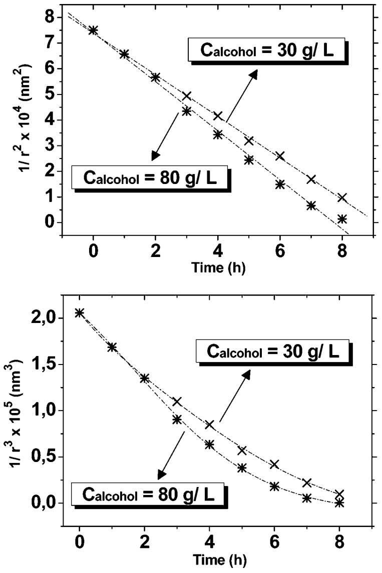


Figure 5. $1/r^2$ and $1/r^3$ as a function of time for experiments M1 (×) and M3 (∗) (Table 3).

Surprisingly, PS-*b*-PEO-based NB miniemulsions were also destabilized by addition of larger amount of butanol, indicating that the medium becomes a better solvent for the stabilizing chains as the concentration in alcohol is increased.

Experiments were thus carried out without butanol (experiments M5 and M6, Table 3), but low monomer conversions (<16%) were obtained in the latter case due to the lack of activity of ruthenium trichloride alone.

For a better insight into the mechanism occurring in absence and presence of butanol, M1 and M5 latexes have been characterized by size exclusion chromatography (SEC) (Figure 6). M1 actually exhibited a bimodal distribution of molar masses (Figure 6B), indicating the formation of two kind of populations by “initiator”. The peak corresponding to low molar mass oligomers may be attributed to NB polymerization initiated by free $RuCl_3$. Indeed, the latter is known to generate polymers of low molar masses, as evidenced by M5, a latex obtained by $RuCl_3$-initiated NB miniemulsion polymerization—without alcohol—which resulted in the formation of large amount of oligomers (Figure 6A). On the other hand, polymer chains of higher molar masses may be generated (M1), provided by the very active metal−hydride species resulting from the reaction of $RuCl_3$ with butanol (Scheme 1).

To reduce the proportion of oligomers in the latex, experimental conditions have been modified to generate more metal−hydride active species. In a first approach, 1.5 equiv of NB was added directly to a $RuCl_3$−butanol

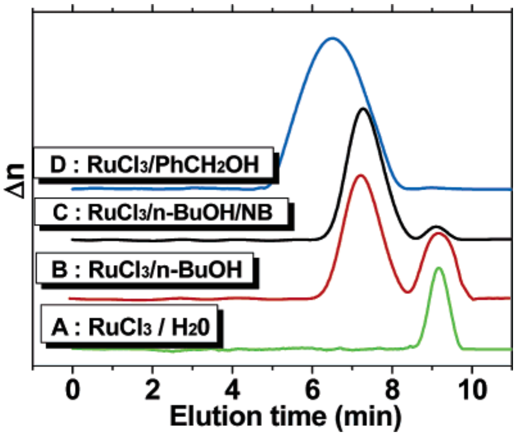


Figure 6. SEC traces of polynorbornene obtained by miniemulsion ROMP (A: experiment M5 ($\overline{M}_n$ = 600 g/mol, PDI = 1.1); B: experiment M1 ($\overline{M}_{n,1}$ = 600 g/mol, PDI_1 = 1.1, $\overline{M}_{n,2}$ = 14 000 g/mol, PDI_2 = 1.6); C: experiment M11 ($\overline{M}_{n,1}$ = 600 g/mol, PDI_1 = 1.1, $\overline{M}_{n,2}$ = 14 000 g/mol, PDI_2 = 1.7); D: experiment M7 ($\overline{M}_n$ = 70 000 g/mol, PDI > 2), Table 3).

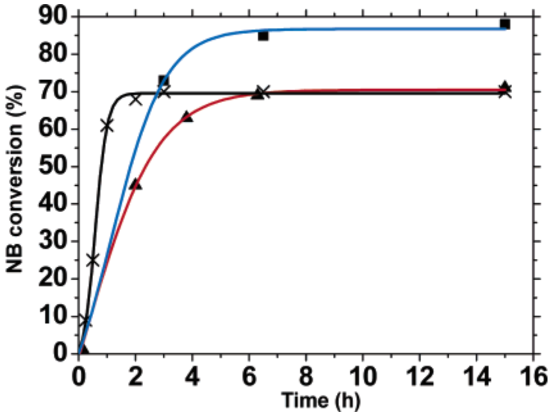


Figure 7. Kinetic results for miniemulsion ROMP of NB (experiment M1, ▲; M11, ×; M7, ■; Table 3).

mixture before being heated to 60 °C for 30 min (experiment M11, Table 3). In this way the metal−hydride/metal−carbene equilibrium reaction (Scheme 1) could be shifted toward the formation of the latter. In addition, metal−carbene species are less hydrophilic compared to metal−hydride or $RuCl_3$ and may diffuse faster to monomer droplets. Accordingly, polymer chains obtained under the condition (Latex M11) exhibited one major population of high molar mass polymers with only some traces of oligomers (Figure 6C). A kinetic study confirmed that the NB conversion was much faster when initiated with “metal carbene” (experiment M11) than with “metal hydride” (experiment M1) (Figure 7).

The second approach consisted of the substitution of 1-butanol for benzyl alcohol as cocatalyst. Indeed, it has been shown[21] that $PhCH_2OH$ gives rise to a more active initiating system than alkyl alcohols such as 1-butanol. As expected, the use of $PhCH_2OH$ considerably enhanced the conversion of NB from 70% to 90% (experiments M7 and M8, Table 3) through higher yield in metal−hydride and allowed the formation of only polymer chains as shown in SEC traces (Figure 6D). The kinetic study revealed that the rate of polymerization of NB is faster than in the presence of 1-butanol but lower than with “metal−carbene” (Figure 7). Nevertheless, the miniemulsion obtained under these conditions with PS-*b*-PEO surfactant as stabilizer (experiment M8, Table 3) was unstable and resulted in a total phase segregation (coagulation) in less than 5 min, likely because of the solubility of PS-*b*-PEO in benzyl alcohol even at low concentration. The last parameter finally examined was the catalyst concentration: with higher amount of the latter the monomer conversion increased as expected from 70% to 76% with SDS (experiment M9, Table 3) and 68% to 74% with PS-*b*-PEO (experiment M10, Table 3).

In general, polymer chains forming these latex particles exhibit rather low molar masses ($\overline{M_n}$ = 15 000 g/mol, Figure 6) and broad distributions (PDI = 1.6), in agreement with previous results obtained with this type of catalyst.

Conclusion

Polynorbornene particles were generated by miniemulsion ring-opening metathesis polymerization. Because of its strong hydrophobic character and high reactivity, well-defined ruthenium carbene ($(PCy_3)_2Cl_2Ru{=}CHPh$) was found to produce PNB coagulum in large amount, but the latter extent could be reduced using a miniemulsion of this initiator. Particles ranging from 200 to 500 nm were generated through this way. Coagulation in NB polymerization could be avoided by using $RuCl_3$ in alcoholic solution. Particles with good stability ranging from 200 to 500 nm were obtained as characterized by DLS. By forming in situ metal−carbene type species the conversion in NB could be increased from 16% to 90%.

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