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Bicompartmentalized Polymer Particles by Tandem ROMP and ATRP in Miniemulsion

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ABSTRACT: This study describes an original approach to prepare biphasic particles by simultaneous ring-opening metathesis polymerization (ROMP) of norbornene and atom-transfer radical polymerization (ATRP) of methyl methacrylate under miniemulsion conditions. A single water-soluble ruthenium macrocatalyst was used to initiate ROMP and mediate ATRP. All situations led to high conversions, and well-distributed particles containing two incompatible homopolymers grown under controlled conditions could indeed be prepared.

Introduction

Many biological structures, such as cells, contain several compartments that condition their physical properties. Such a degree of sophistication is hardly reproduced in conventional synthetic colloidal structures. One way to compartmentalize particles is to rely on the incompatibility of most polymer pairs to induce internal phase separation. Thus, two immiscible polymers must be introduced in the same particle. A competition between thermodynamic and kinetic contributions will then lead to original morphologies such as core−shell, hemispherical, or more complex occluded structures.[1–5] Polymer binary blend particles are usually prepared by seed emulsion polymerizations or by releasing an organic solvent from polymers/solvent droplets dispersed in an aqueous solution of emulsifier. However, the mentioned preparation routes involve time-consuming multistage procedures.

In this work, we explore an alternative approach to generate internally compartmentalized particles that is based on the simultaneous polymerizations of two monomers in miniemulsion. The main advantage of such a route is its straightforwardness: both polymerizations occur simultaneously in the monomers droplets, and no intermediate purification step is required. This technique allows one-pot access to particles composed of two polymers confined in a closed domain of a few hundreds of nanometers. How do the two polymers coexist inside such latices and what kind of morphologies are formed are questions we will attempt to answer. In our investigation, norbornene (NB) and methyl methacrylate (MMA) were polymerized by ring-opening metathesis polymerization (ROMP) and atom-transfer radical polymerization (ATRP), respectively. Both polymerization processes are tolerant of water and could normally be conducted—under appropriate conditions—in a controlled fashion.

Recently, we reported the synthesis of particles uniquely composed of polynorbornene by miniemulsion ROMP promoted by an "ill-defined" initiating system ($RuCl_3 \cdot xH_2O$ in alcohol).[6] Because of the slow kinetics and the poor control over the reaction, we changed the initiator to a "well-defined" one, known to be more efficient: the first generation Grubbs catalyst $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (GC1, see Scheme 1 for its structure). This ruthenium alkylidene is both very active and strongly hydrophobic, so its direct use for miniemulsion ROMP led to a large coagulum. To get rid of this effect, the complex was made water-soluble by inserting a α-norbornenyl poly(ethylene oxide) macromonomer into its alkylidene structure (Scheme 1). Thanks to this new water-soluble macrocatalyst (GC1−PEO_3, three PEO-macromonomer units grafted onto GC1), nice particles were prepared and monomer conversions close to unity were reached.[7] Khosravi and co-workers also prepared a water-soluble ruthenium alkylidene by grafting a PEO chain on the carbene double bond of the ruthenium alkylidene.[8] Other attempts were all based on changing phosphine ligands around the ruthenium center for hydrophilic ones.[9–12]

The report by Simal et al.[13–15] that the first generation Grubbs catalyst—which was initially developed for metathesis—was also a good candidate to control ATRP prompted us to investigate the tandem combination of ROMP and ATRP in miniemulsion. In the presence of our macrocatalyst, both polymerizations occur simultaneously within the droplets. To the best of our knowledge, a one-pot, one-step, one-catalyst approach has never been reported in dispersed media. Although Landfester and co-workers already used miniemulsion polymerization to prepare hybrid latices made of polymer blends, the polymerization mechanisms were completely different and the route proceeded into two steps (successive polymerizations).[16,17] In their case, polycondensation was combined with conventional radical polymerization to synthesize polyurethane/polystyrene (or polybutylacrylate) particles. Concerning the combined use of ROMP and ATRP, only a few one-pot, one-catalyst routes, carried out in solution, are reported.[18–20]

Experimental Section

Materials. All manipulations were performed under a prepurified nitrogen atmosphere using standard Schlenk techniques. Methyl methacrylate (Aldrich, 99% (GC)) and norbornene (Aldrich, 99% (GC)) were dried over calcium hydride and sodium, respectively, and cryo-distilled prior to use. Water was deionized on milli-Q and subsequently degassed by nitrogen bubbling. Toluene, dichloromethane, and pentane were dried over calcium hydride and subsequently cryo-distilled. Polyoxyethylene(100) stearyl ether (Brij700, Aldrich), hexadecane (Aldrich, anhydrous 99+%), ethyl 2-chloropropionate (Aldrich, 97%), and methyl 2-bromopropionate (Aldrich, 98%) were used as received without further purification. (Bis(tricyclohexylphosphine)benzylidine)ruthenium(IV) chloride (first generation Grubbs Catalyst, Aldrich) was stored in a glovebox filled with argon prior to use.

Synthesis of the Water-Soluble Macrocatalyst GC1−PEO_3. The macrocatalyst synthesis proceeds in two steps. First, α-norbornenyl poly(ethylene oxide) macromonomer was synthesized in a previous step by anionic polymerization from 5-norbornene-2-methanol, as previously published.[21] The prepared polymer had a number average molar mass of 4400 $g \cdot mol^{-1}$ (from NMR measure-

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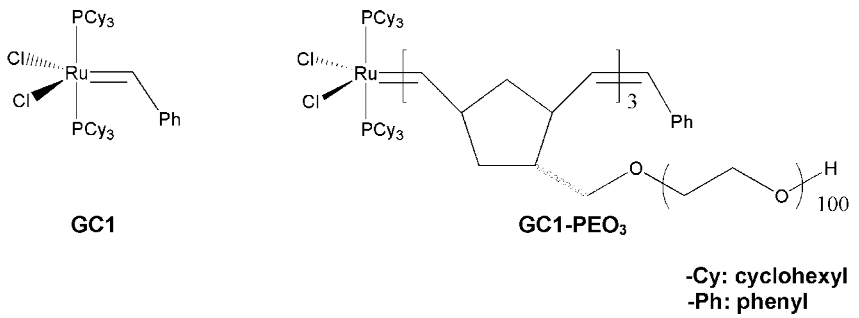
Scheme 1. Structures of the Ruthenium Alkylidenes Used in This Study as Both ROMP Initiators and ATRP Catalysts[a]



[a] Key: (GC1) first generation Grubbs catalyst; (GC1−PEO$_3$) water-soluble macrocatalyst.

ment) and a dispersity of 1.1 (as measured by size-exclusion chromatography, calibrated with PEO standards).

The macromonomer−oligomerization using Grubbs catalyst as initiator led to the water-soluble macrocatalyst, as reported in a previous article.[7] In our case, the synthesis features were chosen so as to target an insertion of three PEO macromonomers per Grubbs catalyst molecule. The overall yield reached 86%, as evaluated by comparing the weight of recovered macrocatalyst to the theoretical one. The almost complete consumption of the macromonomer was evidenced by size exclusion chromatography. The conversion of GC1 to GC1−PEO$_3$ was checked by NMR (shift of the alkylidene proton signal from 19.9 ppm for GC1 to 19.0 ppm for GC1−PEO$_3$). Size exclusion chromatography enabled us to characterize the dispersity of the macrocatalyst (index: 1.2) and to check the high conversion of the macromonomer.

Miniemulsion Polymerization. In a typical recipe (experiment 2b, see Table 1), the aqueous phase was prepared by dissolving the stabilizer Brij700 (0.050 g, 1.1 10^{-5} mol) in degassed deionized water (50 mL). In a separate container, MMA (2.1 mL, 2×10^{-2} mol) was added to hexadecane (0.13 mL, 4.4×10^{-4} mol, 5 wt. % of the MMA) and ethyl 2-chloropropionate (5 μL, 3.9×10^{-5} mol). This organic phase was then degassed by means of three freeze−pump−thaw cycles and added under stirring and nitrogen atmosphere to the aqueous phase. The pre-emulsion was then temporarily stored under vacuum and homogenized via high shear agitation (2 min) and magnetic stirring (at least 1 h). The miniemulsion was finally obtained by ultrasonication of the pre-emulsion (probe SONIC; maximal power, 750 W; sonication, power 50% for 2 min; Schlenk immersed in a cooling bath at 0 °C) and transferred to a double-wall reactor equipped with a nitrogen inlet, a mechanical stirrer, and a condenser. Prior to this transfer, the reactor was purged with nitrogen. To trigger the polymerization, an aqueous solution containing the macrocatalyst (0.230 g, 1.7×10^{-5} mol, dissolved in 3 mL of degassed deionized water) was introduced to the preheated miniemulsion (60 °C). This last addition marked the time zero of the reaction.

For experiments 1a−1e using Grubbs catalyst instead of the macrocatalyst, the ruthenium alkylidene complex was initially dissolved in the organic phase and the time zero corresponded to the transfer of the miniemulsion to the preheated reactor.

For experiments involving the ROMP of NB alone or combined with ATRP, the procedure remains the same. The total amount of monomers is maintained constant (2×10^{-2} mol).

Solution Polymerization. In a typical experiment (entry 1a of Table 1), MMA (2.1 mL, 2×10^{-2} mol), first generation catalyst (14 mg, 1.7×10^{-5} mol), and ethyl 2-chloropropionate (5 μL, 3.9×10^{-5} mol) were dissolved in toluene (2 mL). After three freeze−pump−thaw cycles, the polymerization was started by immersing of the Schlenk tube in an oil bath, which had been previously heated to the chosen temperature (60 °C). After 6 h, the radicals were quenched using hydroquinone.

Nuclear Magnetic Resonance (NMR). ^{1}H NMR studies were completed thanks to a Bruker spectrometer 400 MHz, in CDCl$_3$ at 25 °C.

Kinetic Studies. During kinetics studies, monomers conversions were followed via gas chromatography (GC). The device was composed of a hydrophobic capillary column (BP1−30m) coupled to a FID detector (VARIAN 33, 650). Analysis conditions were the following: vector gas: N$_2$, $T_{\text{injector}} = 250$ °C, $T_{\text{detector}} = 280$ °C, and column temperature profile has $T_{\text{initial}} = 50$ °C for 2 min and then linear increase (10 °C·min^{-1}).

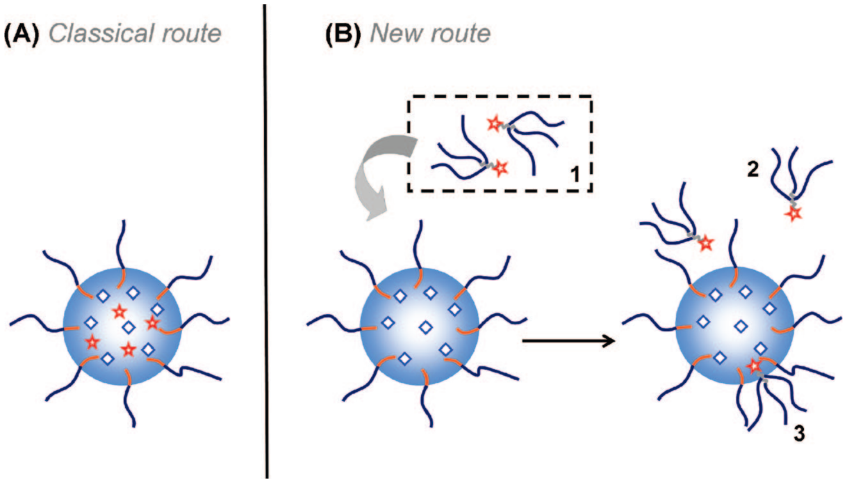
At given times, miniemulsion aliquots were dissolved in a tetrahydrofuran (THF) solution containing ATRP and/or ROMP deactivators: hydroquinone and ethyl vinyl ether, respectively. Shortly after the dissolution, the solution was immersed into liquid nitrogen in order to quench the reaction and eventually stored in the refrigerator before injection. For miniemulsion polymerization,

Table 1. Ruthenium-Catalyzed Polymerizations of Methyl Methacrylate[a]

entry	medium[b]	catalyst	initiator[c]	[MMA]$_0$/ [initiator]$_0$/ [Ru]$_0$	conversion[d] (%)	M_n[e] (g·mol^{-1})	M_w/M_n[e]	f[f]	d_g[g] (nm)	d_p[g] (nm)
1a	solution	GCl	Cl	513/1/0.44	59	28900	1.7	1.0		
1b	miniemulsion A	GCl	Cl	513/1/0.44	99	81900	2.9	0.6	192	169
1c[h]	miniemulsion A	GCl	Cl	513/1/0.44	97	74700	1.8	0.7	203	202
1d[i]	miniemulsion A	GCl	Cl	513/1/0.44	77	46800	3.3 (bimodal)	0.8		182
1e	solution	GCl	Br	455/1/0.39	64	28400	1.4	1.0		
2a	solution	GCl−PEO$_3$	Cl	513/1/0.42	41	56900	1.6	0.4		
2b	miniemulsion B	GCl−PEO$_3$	Cl	513/1/0.42	96	66600	2.4	0.7	189	204
2c	miniemulsion B	GCl−PEO$_3$	Br	455/1/0.39	94	65600	2.0	0.7	195	170
2d	miniemulsion B	GCl−PEO$_3$	Cl	513/1/0.77	94	46700	1.8	1.0	191	198
2e	miniemulsion B	GCl−PEO$_3$	Cl	513/1/0.19	92	65500	2.3	0.7	195	201

[a] Conditions: N$_2$ atmosphere; 60 °C, 6 h. [b] Solution: in toluene. Miniemulsion: A = classical route: GC1 initially dissolved in the monomer droplets; B = new route: water-soluble GC1−PEO$_3$ added to preformed monomer miniemulsion. [c] ATRP initiator: Cl = ethyl 2-chloropropionate/Br = methyl 2-bromopropionate. [d] methyl methacrylate (MMA) conversion determined by GC. [e] Number-average molar mass and polydispersity index determined by SEC. Calibration with PMMA standards. [f] Initiation efficiency $f = M_{n,th}/M_{n,exp}$ with $M_{n,th} = [\text{monomer}]_0/[\text{initiator}]_0 \times \text{MW(monomer)} \times \text{conversion}$. [g] Z-average droplets and particle hydrodynamic diameters as measured by DLS. [h] In experiment 1c, toluene has been added to the organic phase. [i] In experiment 1d, ultrasonication duration has been extended from 2 to 12 min.

Scheme 2. Comparison of Both Routes Followed To Perform ATRP in Miniemulsion[a]



[a] Key: (A) In the route classically used to carry out ATRP in miniemulsion, the ATRP initiator (◆) and the control agent (☆, here Grubbs catalyst of the first generation) are both initially present in the droplets and the polymerization is thermally started. (B) In the new approach, only the ATRP initiator is present in the droplets so the polymerization can not start. The metal complex—which has been made water-soluble—is subsequently added as aqueous solution after the miniemulsion has been prepared (1). The amphiphilic complexes will then migrate through the dispersing phase (2) to finally penetrate the droplets (3) and trigger off the polymerization. Only this approach, where the catalyst is initially outside the droplets, is suitable to perform ATRP, ROMP, and their tandem combination.

hexadecane was used as internal standard. In case of solution reactions, this role was played by toluene.

Molar Mass Distributions. Molar mass distributions (MMD) and number average and weight average molar masses (M_n and M_w, respectively) were determined by size exclusion chromatography (SEC) using THF as mobile phase (flow rate: 1.0 mL·h^{-1}). The apparatus was composed of three TOSOH Bioscience TSKgel columns [G4000Hxl (particle size, 5 μm; pore size, 200 Å; exclusion limit, 400000 Da), G3000Hxl (particle size, 5 μm; pore size, 75 Å; exclusion limit, 60000 Da), G2000Hxl (particle size, 5 μm; pore size, 20 Å; exclusion limit, 10000 Da)] equipped with a JASCO HPLC pump type 880-PV linked to a Varian refractive index (RI) detector and a JASCO 1575 UV/vis absorption detector. Calibrations were performed with polystyrene and PMMA standards.

Droplet and Particle Size Measurements. Droplet and particle hydrodynamic sizes and distributions were determined by dynamic light scattering (DLS) on a Malvern Zetasizer 3000. Each measurement was composed of 3 runs of 300 s and carried out at a fixed scattering angle of 90°. In order to minimize multiple scattering, the miniemulsion (or the mini-latex) was diluted (roughly 100 times) in an aqueous solution saturated with monomers and Brij 700. Autocorrelation functions were first analyzed using the cumulant method and systematically reanalyzed thanks to the CONTIN algorithm in order to check the presence of multimodal distributions.

Particle Morphologies. Latex particle morphologies were observed by transmission electron microscopy (TEM) using a Hitachi H7650 microscope operating at 80 kV. One droplet of latex sample was deposited on a 200 mesh carbon-coated copper grid and left to dry under the hood. The samples containing PMMA were stained by dipping the grid in a 1 wt % aqueous solution of ammonium molybdate.

Results and Discussion

A previous paper[22] briefly presented the use of tandem ROMP and ATRP to prepare architectures (star- and comblike copolymers) within miniemulsion droplets. Instead of directly coupling the two distinct polymerizations, the current work first focuses on miniemulsion ATRP using the newly developed macrocatalyst (GC1−PEO$_3$). The tandem combination is then examined in a second part. As Ru-catalyzed miniemulsion ATRP has not been reported yet, the activity of this macrocatalyst was compared with that of its precursor: Grubbs catalyst of first generation (GC1). However, with the latter being hydrophobic, it could be used via a conventional miniemulsion route, with the monomer, the initiator, and the catalyst being present in the droplets from polymerization onset. At the opposite end, the use of the water-soluble macrocatalyst required an unconventional approach. The differences between these routes are illustrated in Scheme 2 and described hereafter.

In the conventional route, all the components required to carry out ATRP (ATRP initiator, metal complex catalyst, and monomer) were initially dissolved in an organic phase, and then mixed with an aqueous phase and ultrasonicated. Polymerization was triggered upon heating. This approach has been extensively investigated in the case of Cu-catalyzed miniemulsion ATRP[23–26] but never with ruthenium.

Contrary to the previous approach, with GC1−PEO$_3$ as catalyst, the metal complex was not present in the initial droplets. And therefore, no reaction could occur because both initiator and metal complex are required to generate radicals and trigger ATRP. When added to the aqueous medium, this water-soluble macrocatalyst migrates through the dispersing phase, penetrates the droplets due to its amphiphilic nature and promotes the polymerization. As GC1−PEO$_3$ can be added to the reaction medium after the preparation of the droplets, it is suitable for both ROMP and ATRP carried out separately or in tandem. Unlike GC1−PEO$_3$, GC1 is not appropriate for ROMP under miniemulsion conditions and served only here as reference to check whether GC1−PEO$_3$ could bring about ATRP.

1. Formulation and Stability of Monomer Miniemulsions.

A miniemulsion is a specific dispersed medium, in which a pseudosteady state is reached through the minimization of two phenomena.[27] The first, named Ostwald ripening is a diffusional degradation which can be entirely counterbalanced by the presence of an ultrahydrophobic agent in the droplets. The second, coalescence, is well-known in dispersed media and commonly avoided by addition of surfactants. In miniemulsions, the interface coverage by surfactant molecules is not complete, and therefore, the final state may not be thermodynamically stable. However, with an appropriate formulation, the miniemulsion can remain stable for a long time. In that case, one considers that there is no diffusion of monomers (or other compounds) through the continuous phase, which means that no exchange occurs between the droplets. As a result, each

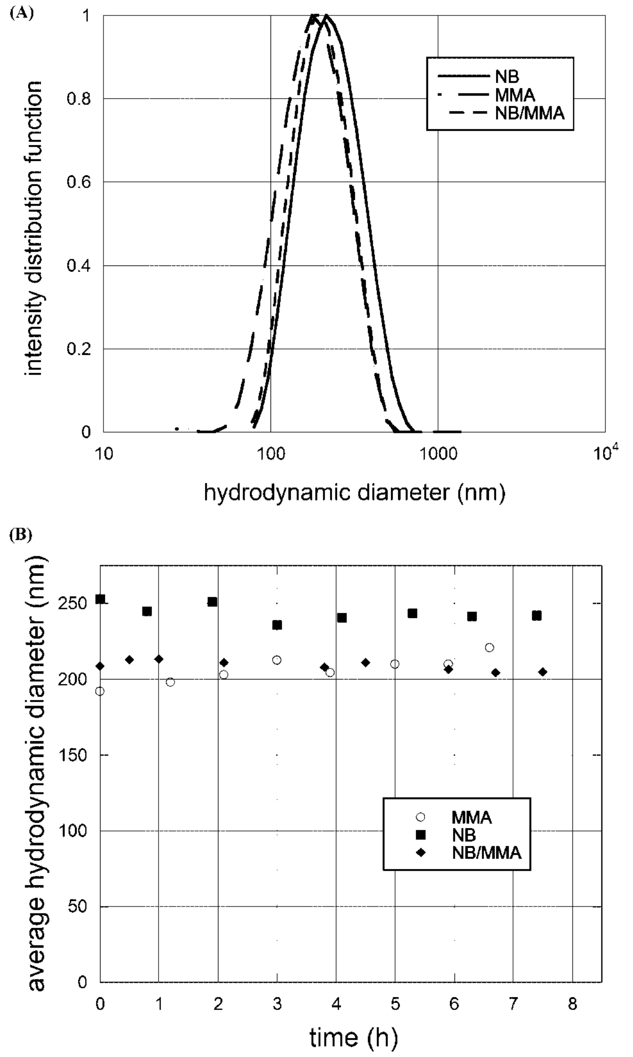


Figure 1. Monomer miniemulsions formulated with Brij700 as surfactant and hexadecane as hydrophobic agent. (A) Droplet size distributions for methyl methacrylate, norbornene and methyl methacrylate/norbornene (molar ratio: 50/50) miniemulsions, as determined by dynamic light scattering. The given distributions are obtained with the formulation detailed in the experimental section and correspond to the state reached just after sonication. (B) Time stability of the previous miniemulsions.

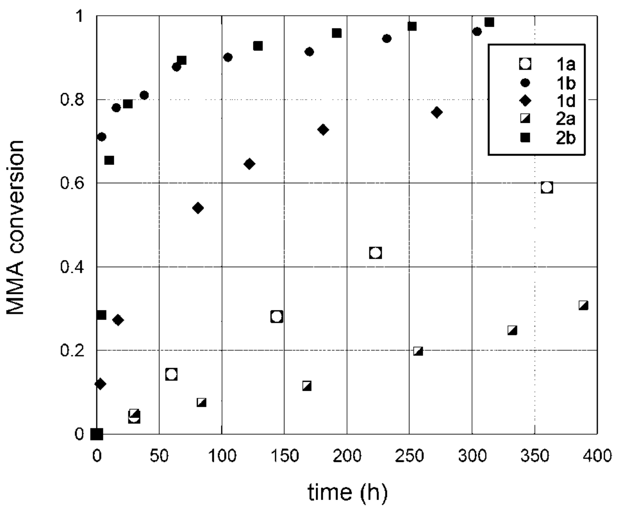


Figure 2. Conversion versus time plot for selected miniemulsion ATRP of MMA: experiment 1a, solution ATRP with GC1; experiment 1b, miniemulsion ATRP with GC1; experiment 1d, miniemulsion ATRP with GC1 (sonication duration increased from 2 to 12 min); experiment 2a, solution ATRP with GC1−PEO$_3$; experiment 2b, miniemulsion ATRP with GC1−PEO$_3$. See Table 1 for further details concerning the experiments.

droplet behaves as an isolated "mini-reactor" and the particles must be one-to-one copies of the droplets.

In such a miniemulsion, the choice of the surfactant must be made with care. Grubbs and co-workers indeed observed a possible halogen ligand exchanges around the ruthenium of GC1.[10,28] Actually, they noticed that the use of bromide salts surfactants (dodecyltrimethylammonium bromide, DTAB) has a negative effect on the activity of GC1. They thus preferred to use a chlorinated surfactant such as dodecyltrimethylammonium chloride (DTAC). In the latter case, halogen exchange between the surfactant and the Grubbs catalyst has no effect on their structures (both ligands are chloride). Furthermore, as we showed in a previous study, diblock-copolymers are more suitable than sodium dodecylsulfate (SDS) for the stabilization of NB miniemulsions.[6] Consequently, we opted in this work for Brij700, a neutral diblock copolymer consisting of an aliphatic C18 chain and a PEO block (~100 monomer units). Hexadecane was used as costabilizer (hydrophobic agent). Stability studies of MMA and NB miniemulsions carried out using these conditions are shown in Figure 1. The first diagram indicating the size distribution of the droplets formed just after sonication emphasizes the suitability of the recipe for the preparation of miniemulsions of NB and MMA mixtures. The time-evolutions of the droplets average hydrodynamic diameter, which were followed by DLS, are displayed in Figure 1B. In every cases, it clearly appears that no destabilization occurs during the first six hours which corresponds to the duration of the polymerizations (in the three cases, droplets were still stable after 20 h).

2. Ruthenium-Catalyzed ATRP in Miniemulsion. Two main effects have been investigated first. The results obtained in dispersed medium under miniemulsion conditions were compared with those generated in solution, and the suitability of the two Grubbs catalyst—GC1 versus its modified version GC1−PEO$_3$—was checked. Indeed if, strictly speaking, miniemulsion corresponds to a bulk system that has been compartmentalized, solution constitutes a homogeneous medium which is more convenient to study (especially kinetics) and has thus been preferred. The model reaction chosen for the investigation is the free-radical polymerization of methyl methacrylate (MMA) initiated by either ethyl 2-chloropropionate or methyl 2-bromopropionate in the presence of GC1 or GC1−PEO$_3$. The results obtained with different experimental conditions are given in Table 1 and Figure 2. The ratio [halogenated initiator]$_0$/[catalyst]$_0$ (approximately 1/0.4 for most of the experiments) has been chosen based on the work published by Simal et al. about solution ATRP of MMA using Grubbs catalyst (ratio: 1/0.5).[13]

2.1. Conventional Route: ATRP with (Hydrophobic) Grubbs Catalyst of First Generation. The activity of GC1 as ATRP catalyst was first examined in toluene solutions with a chlorinated initiator (ethyl 2-chloropropionate, experiment 1a in Table 1). After 6 h, the MMA conversion reached 59% and the number average molar mass was close to the targeted value (*f* close to unity), but the molecular weight distribution (MWD) was broader than those usually obtained with copper or classical ruthenium ATRP catalysts.[29]

The miniemulsion polymerization was then carried out using the classical route described above (experiment 1b). Well-defined particles were obtained without any noticeable aggregate or coagulum. Not surprisingly, the kinetics was accelerated, a phenomenon generally attributed to the compartmentalization of the reaction medium. Whereas MMA could not be fully

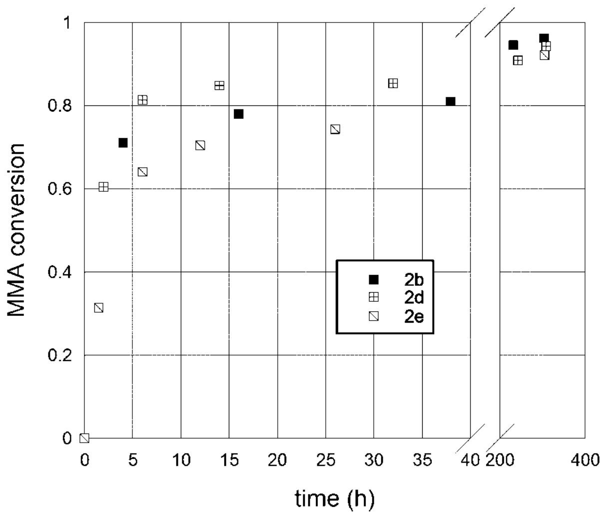


Figure 3. Influence of the initial amount of macrocatalyst (GC1−PEO$_3$) on the start of the miniemulsion ATRP ("new route"). [MMA]$_0$/[initiator]$_0$/[GC1−PEO$_3$]$_0$: experiment 2b, 513/1/0.42; experiment 2d, 513/1/0.77; experiment 2e, 513/1/0.19. For the sake of clarity, lines linking the experimental points are here given as guides for the eyes. See Table 1 for further details concerning the experiments.

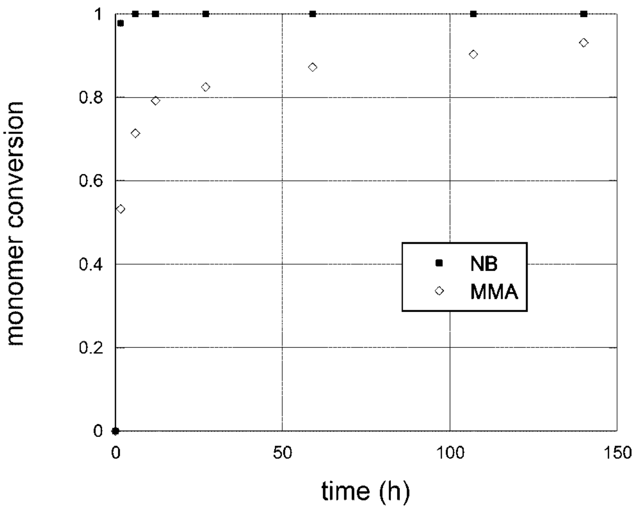


Figure 4. Kinetics follow-up of the ROMP of NB and the ATRP of MMA, performed "simultaneously" under miniemulsion conditions.

consumed in solution polymerization after 6 h at 60 °C, these miniemulsion conditions enabled us to reach, under the same conditions, 99% conversion. However, the obtained polymer exhibited a broad MWD (PDI = 2.9). Two hypotheses could be contemplated to account for lack of control over the polymerization: either GC1 could not properly be dissolved within the monomer droplets (supposed formation of catalyst clusters) and/or the catalyst underwent a partial degradation during sonication.

A small volume of toluene (0.4 mL) was added to the organic phase in an attempt to better solubilize GC1 before its mixture with the aqueous phase (experiment 1c). This addition of toluene resulted in a significant reduction of the PDI. Hence, the hypothesis seems to be confirmed. However, the improved molar weight distribution may also be explained by a decrease of the viscosity inside the droplets, leading to a more suitable environment for polymerization control.

The influence of ultrasonication was also examined upon varying its duration from 2 to 12 min (experiment 1b/1d). In the latter case, the rate of monomer consumption was substantially slower and the final conversion reached a lower value. Moreover, an increase of the polydispersity index was observed. These observations tend to confirm that the ruthenium alkylidene underwent degradation during sonication. This result indicates that even in 2 min sonication, some degradation might have occurred, hence the large PDI observed. Actually, this phenomenon was already reported by Matyjaszewski and co-workers for copper-mediated ATRP. The low oxidation state of copper Cu^{I} being sensitive to ultrasonication (oxidation), the so-called reverse ATRP which starts with the more stable oxidation state Cu^{II} is generally preferred in miniemulsion.[26,30] To avoid the partial degradation of the metal complex during sonication and formulation of the miniemulsion, an amphiphilic water-soluble catalyst such as GC1−PEO$_3$ that can be added after sonication may be contemplated as a new alternative to perform (direct) ATRP in miniemulsion.

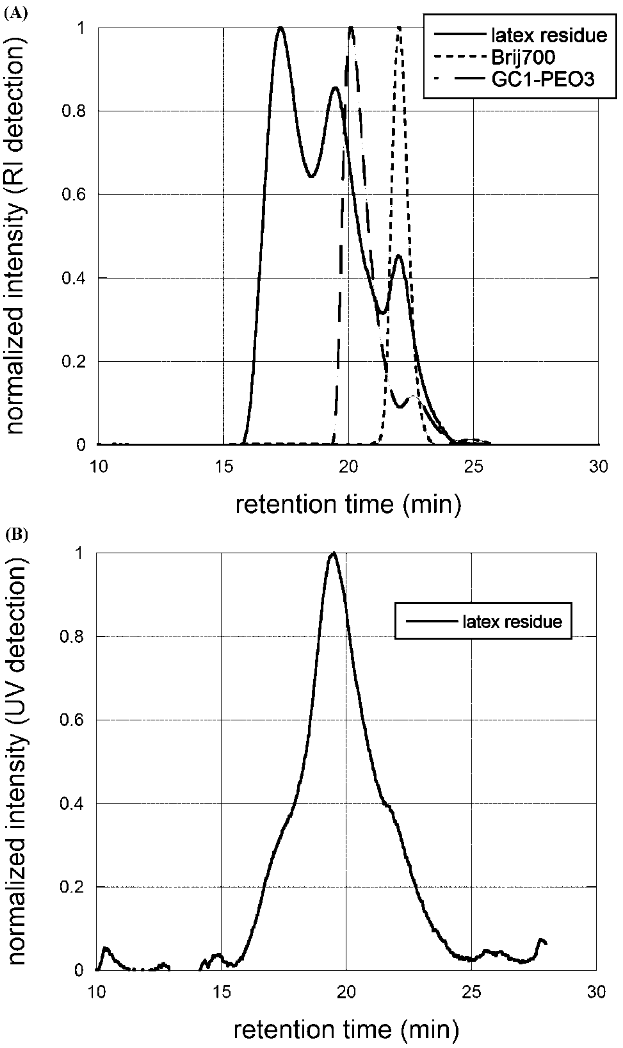
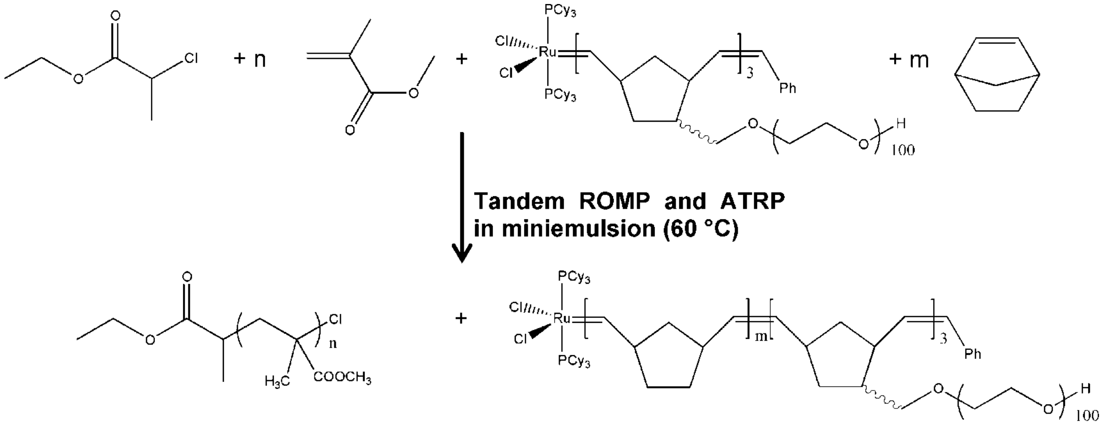


Figure 5. SEC traces concerning the tandem homopolymerizations of MMA and NB in miniemulsion: (A) refractive index detector; (B) UV detector (256 nm). Solid line: reaction medium at the end of the polymerization. Water has been removed under vacuum and the obtained residue has then been dissolved in THF. Dashed dot dot line: macrocatalyst (GC1−PEO$_3$). Dashed line: surfactant (Brij700).

2.2. New Route: ATRP Using the Water-Soluble Macrocatalyst. As in the previous part, the suitability of GC1−PEO$_3$ for ATRP was first checked in toluene solution (experiment 2a). Compared to experiment 1a, the polymerization kinetics was slightly slower and the initiation efficiency smaller ($f = 0.4$). Nevertheless, no significant change was observed with respect to the polydispersity. The steric hindrance induced by the PEO

Scheme 3. One-catalyst Combination of the ROMP of Norbornene with the ATRP of MMA



grafts around the ruthenium alkylidene may well be responsible for the partial efficiency observed.

The use of GC1−PEO$_3$ under miniemulsion conditions resulted in the formation of nice particles with no visible aggregation. The miniemulsion conditions brought about a much faster rate of polymerization as compared to that observed for solution polymerization. After 6 h, the monomer conversion was almost complete (96%). Although the number average molar mass was closer to the expected values than that seen for solution conditions, a broad MWD (polydispersity index: PDI = 2.4) was observed again (experiment 2b). Upon substituting a brominated initiator (methyl 2-bromopropionate) for the previous chlorinated one (ethyl 2-chloropropionate), the PDI could be reduced, but no effect was observed on the initiation efficiency.

As a matter of fact, the reasons for a lower than expected efficiency of the initiator may be found in the water solubility of the macrocatalyst. Indeed, the PEO chains grafted on the ruthenium alkylidene impart such a hydrophilic character to the macrocatalyst that it can at best anchor at the surface of the droplet but certainly not penetrate inside the latter. It is also very likely that a fraction of the macrocatalyst remains dissolved in the continuous phase. As GC1−PEO$_3$ is not fully available for the catalysis of the atom transfer process, this may affect the efficiency of the initiation as illustrated in Scheme 2B. As an attempt to increase the extent of GC1−PEO$_3$ really available for the catalysis within the droplets, a larger amount was then used (experiment 2d). A reduced dispersity of molar masses (PDI = 1.8) and an initiation efficiency close to 1 were observed with a higher [catalyst]$_0$/[initiator]$_0$ ratio. In contrast, reducing the amount of macrocatalyst compared to that used in experiment 2b did not bring about significant change in the initiation efficiency and the dispersity of the polymer formed. In addition, not surprisingly, the higher the initial amount of catalyst, the faster the kinetics of polymerization (Figure 3).

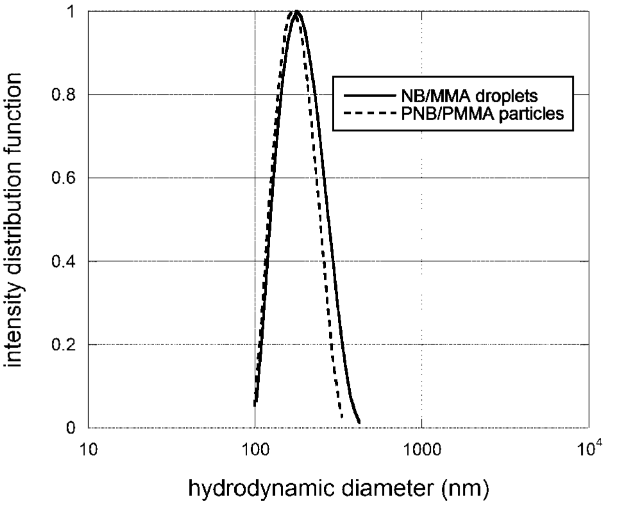


Figure 6. Droplet/particle size distributions for MMA/NB (molar ratio: 50/50) miniemulsion, before (*z*-average hydrodynamic diameter: 207 nm) and after polymerization (*z*-average hydrodynamic diameter: 184).

3. Tandem Combination of ROMP and ATRP in Miniemulsion. Before applying the approach to the tandem combination of the ATRP of MMA with the ROMP of norbornene (NB), it was first applied to the polymerization it has been initially designed for: the ROMP of NB. According to the results previously published, [7] well-defined particles (droplet and particles z-average hydrodynamic diameters: $d_g \approx 229$ nm; $d_p \approx 225$ nm) were obtained via a fast polymerization leading to a high conversion (97%) and a PDI of 1.9. Due to the high reactivity of NB, a 17% coagulation was observed ($\%_{\text{aggregation}} = m_{\text{aggregate}}/(m_{\text{monomer}} + m_{\text{Brij700}} + m_{\text{hexadecane}})$).

The fact that particles of PMMA and PNB could be separately prepared using GC1−PEO$_3$ was an incentive to carry out the simultaneous polymerizations. In the latter case, the ruthenium macrocatalyst acts both as ATRP mediator and ROMP initiator. What should be remembered here is that the ruthenium alkylidene structure is maintained by the ROMP process. Consequently, the ruthenium end-chain of PNB is expected to be still reactive in ATRP all throughout the metathesis reaction. Actually, such dual polymerizations have already been investigated by Grubbs', Novak's, and Wooley's groups in solution.[18–20] Moreover, the presence of NB in the experiment may permit to bring more macrocatalyst molecules to the droplets, insofar as the addition of NB units on the ruthenium alkylidene of GC1−PEO$_3$ must emphasize its hydrophobic character. The simultaneous homopolymerizations of NB and MMA under miniemulsion conditions starting from a 50/50 mixture (monomer molar ratios) resulted in well-defined particles. No aggregation could be noticed and conversions reached 99% and 93% for MMA and NB respectively. Kinetics studies indicated that the intial kinetics of ROMP and ATRP were relatively close (in the resolution limits of our follow-up at least). However, after a few minutes, the consumption of MMA tended to slow down, as shown in Figure 4. In addition, no relevant effect of the tandem feature was observed on the ATRP kinetics (as compared with the ATRP of MMA performed alone: entry 1b of Table 1 and Figure 2). The SEC traces of the latex residue are shown in Figure 5. When comparing the latter traces with those of the surfactant (Brij700) and of the macrocatalyst, three main peaks can be distinguished. From left to right, the first

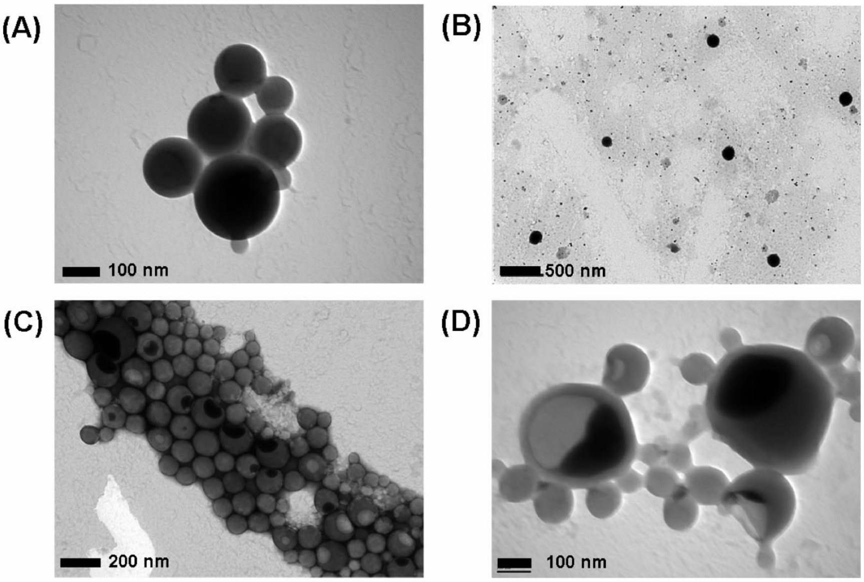


Figure 7. TEM images of (A) PNB particles (unstained), (B) PMMA particles (stained with ammonium molybdate), and (C and D) PNB/PMMA homopolymers blend particles (initial molar ratio NB/MMA: 50/50, stained with ammonium molybdate).

one can be attributed to PMMA homopolymer, the second to PNB homopolymer and the third to the surfactant. These traces may also include a part of the macrocatalyst that remained dissolved in the aqueous phase and the macromonomer left over after the preparation of the macrocatalyst. The distinction between the peaks due to PMMA and PNB can be easily made through the comparison of the traces corresponding respectively to UV and RI detections. As PMMA barely absorbs at 256 nm (wavelength chosen for the UV detector), the peak corresponding to this polymer is the one that exhibits a maximum at a retention time of 17 min (the first one starting from the left). Then, several attempts were made to separate the different components of the mixture and analyze them separately, but all failed. The presence of PEO, with its hydrophilic character, in four of the components (all except PMMA) prevented us in succeeding in our trials to selectively precipitate each polymer Scheme 3.

4. Colloidal Aspect of the Miniemulsion Polymerizations. As previously mentioned, in miniemulsion polymerizations, each droplet behaves as an isolated "mini-reactor" and the particles formed are one-to-one copies of the droplets. All miniemulsion polymerizations described in this study gave rise to well-defined particles with an average hydrodynamic diameter of about 200 nm. Particle average diameters were close to the ones of initial monomer droplets (see Table 1). Therefore, no or little diffusion occurred as expected in a regular miniemulsion process. Figure 6 displays the hydrodynamic diameter distributions of a miniemulsion of NB and MMA (molar ratio: 50/50), before and after polymerization. The similarity between the distributions of the initial droplets and of the resulting particles corroborates the previous comment. Similar results were obtained for all entries of Table 1.

5. Structure of the Particles. Figure 7 exhibits the TEM pictures of PNB particles, PMMA particles and of the hybrid particles composed of the two homopolymers. The PNB latex (Figure 7A) is made of spherical particles whose size distribution is in good agreement with the results obtained from DLS. If PNB is able to absorb electrons, this is not the case for PMMA; therefore, the use of a staining agent (ammonium molybdate) was required to observe PMMA particles. The contours of PMMA particles appear blurred (Figure 7B), compared to PNB particles, indicating a partial spreading of PMMA on the TEM grid. Actually, this phenomenon—likely due to the fact that the latex is in a dry state—was also noticed by Tillier et al. for PMMA latices prepared by emulsion polymerization.[5] For PNB/PMMA blend particles, the use of ammonium molybdate allowed us to stain selectively PMMA and thus to distinguish it from PNB. Parts C and D of Figure 7 clearly show that phase separation occurs within the particles and makes the homopolymers adopt a hemispherical morphology. Actually, the PNB seems to constitute an incomplete outer shell containing PMMA. However, in some cases, the PMMA has been partly or completely expulsed from the PNB shell. These aspects are currently investigated in greater details. It is well-known that particle morphology results from a competition between kinetics and thermodynamics effects.[31] Our miniemulsion approach that starts from binary monomer droplets may bring new original conditions to phase separation.

Conclusions

ROMP and ATRP have been simultaneously carried out in miniemulsion by means of a one-pot, one-step, one-catalyst approach. Despite substantial mechanistic differences involved in both polymerization processes, the Grubbs catalyst-based ruthenium alkylidene played the roles of ROMP initiator and ATRP catalyst. Both polymerizations reached conversions close to unity with faster kinetics compared to solution ones. In spite of the heterogeneity of the reaction medium and the requirements of ROMP, suitable experimental conditions could be found to perform ATRP and obtain polymers with satisfactory dispersity (PDI $\sim$ 1.8) and initiation efficiency ($\sim$1). After demonstrating the feasibility of the simultaneous polymerizations of MMA and NB, this study clearly showed the formation of Janus-type particles with the two homopolymers segregating in two hemispheres. The scope of this discovery is further explored with the view of developing original applications.

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