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Simultaneous ROMP and ATRP in Aqueous Dispersed Media: A Straightforward Strategy to Prepare Polymer Composite Particles with Original Morphologies

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Summary: The simultaneous ring-opening metathesis polymerization of norbornene and atom-transfer radical polymerization of methyl methacrylate is used as a convenient tool to prepare polymer composite particles in a single step and using a single catalyst. The current article reviews the use of miniemulsion and microemulsion conditions to reach this goal. The two developed approaches are assessed on chemical and colloidal levels and the prepared composite particles are scrutinized from a morphological point of view.

Keywords: atom-transfer radical polymerization (ATRP); microemulsion polymerisation; miniemulsion polymerization; polymer composite particles; ring-opening metathesis polymerization (ROMP)

Introduction

To broaden the scope of applications of polymer composite latices in paints,[1] coatings and impact-resistant plastics,[2] many investigations have been devoted to their preparation over the past decades. The particles of these latices are composed of at least two polymers which are subjected to phase separation ruled by a competition between thermodynamic contribution (incompatibility of most polymer pairs) and kinetic factors (chain mobility). By tuning the synthesis conditions, original morphologies including core-shell, hemispherical and complex occluded structures (raspberry-like, onion-like, octopus-like) can now be readily prepared.[3–7]

Because polymer composite particles are composed of several materials, their preparation of polymer composite particles generally proceeds via time-consuming multistep procedures, for instance dispersion of preformed polymers[6,8] or seed emulsion polymerization.[3,9] This article reviews two approaches, based on a new straightforward one-step, one catalyst strategy, to polymer composite particles consisting either of homopolymer blends or of graft-copolymers. The principle of this development is a combination of two simultaneous mechanistically different polymerizations in aqueous dispersed media. Norbornene (NB) and methyl methacrylate (MMA) were converted to the particles *via* ring-opening metathesis polymerization (ROMP) and atom-transfer radical polymerization (ATRP), respectively. Both polymerizations can be carried out simultaneously using first-generation Grubbs catalyst, $[RuCl_2(PCy_3)_2=CH\text{-}Ph]$ (**GC1**), to promote ROMP and control ATRP, as already reported for the synthesis of block and graft copolymers in solution.[10–12] Nevertheless, in our conditions, the extension of such combination to aqueous dispersed media is made difficult by a strong activity of **GC1** towards the

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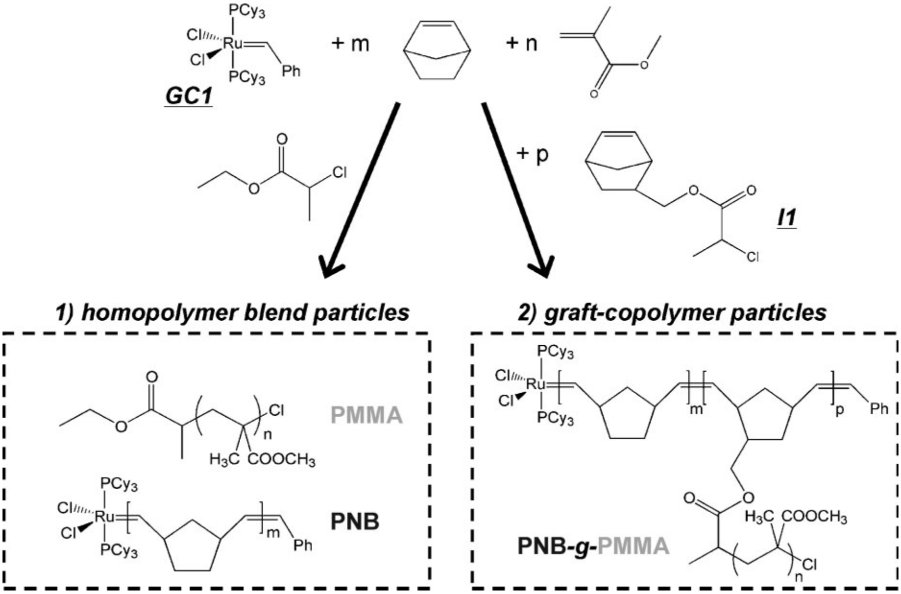
ROMP of NB. As soon as the catalyst is in contact with NB, a fast polymerization occurs even at room temperature. From the practical point of view, this means that the catalyst can not be dissolved directly in the monomer phase that has to be subsequently dispersed in water. On the other hand, because of its hydrophobic nature, adding **GC1** to aqueous monomer dispersions is problematic. Besides, **GC1** as dual catalyst is also the mediating agent of ATRP. Thus, its initial presence outside the monomer droplets seems inadequate. In spite of these constraints, there is no other way of combining ROMP and ATRP in a tandem fashion in aqueous heterogeneous media. The two distinct original routes detailed in this article were designed to fulfil the previous requirements. Both make it possible to prepare either homopolymer blend particles or graft-copolymer particles (using an inimer, **I1**), as illustrated in Scheme 1. Their examinations were conducted both on chemical and colloidal levels.

First Route: Modification of GC1 Towards Water-Solubility to Perform Simultaneous ROMP and ATRP in Miniemulsion

Working under miniemulsion conditions appears as one of the most elegant ways to achieve simultaneous ROMP and ATRP in aqueous dispersed media. A miniemulsion is a pseudo-steady heterogeneous medium stabilized using a surfactant (against coalescence) together with a hydrophobic agent (against Ostwald ripening). The conditions are chosen so as to avoid the formation of surfactant micelles in the dispersing phase. Consequently the droplets are the single *loci* available for the reaction. During miniemulsion polymerizations, once droplets have been nucleated, the peculiar stabilization enables to avoid inter-droplets exchanges. As a result, each droplet behaves as an isolated "minireactor" and the particles must be one-to-one copies of the droplets. The last frame appears particularly suitable when ATRP is



Scheme 1.
One-catalyst, one-step combination of ROMP and ATRP for the preparation of polymer composite particles. Under miniemulsion conditions **GC1** is modified before use, so the polynorbornene chain-ends are functionalized differently (see Scheme 2).

involved because this polymerization technique implies several components (monomer, alkyl halide initiator, control agent/catalyst) which have different diffusivities. Under conventional emulsion conditions, after nucleation, the monomers and the other organic compounds diffuse through the aqueous phase from large "reservoir droplets" to the growing particles. Consequently, their concentrations within the reaction locus (growing particles) undergo a continuous evolution. Miniemulsion conditions enable to eliminate this phenomenon, which is particularly problematic for ATRP.[13–15] The results obtained for the syntheses performed in this dispersed medium are summarized in Table 1. In our conditions, the stabilization was ensured by Brij700® (*surfactant*, polyoxyethylene (100) stearyl ether, Aldrich) and hexadecane (*hydrophobe*).

The investigation was started with NB miniemulsion **GC1** being both very active and strongly hydrophobic, its direct dropwise addition (after dilution with toluene) led to a large amount of coagulum, as published in a previous paper.[16] To get rid of this effect, the complex was made water-soluble by inserting α-norbornenyl-poly(ethylene oxide) macromonomers in its alkylidene structure (Scheme 2). Thanks to this new water-soluble macrocatalyst (**GC1-PEO**), nice particles were prepared with limited coagulation ($\%_{\text{coagulation}} = m_{\text{coagulate}}/(m_{\text{monomer}} + m_{\text{Brij700}} + m_{\text{hexadecane}}) = 17\%$) and monomer conversions close to unity were obtained.[17]

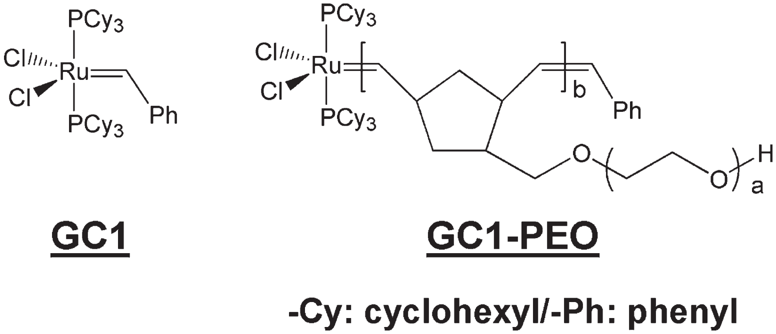
As a second step, the suitability of the use of **GC1-PEO** to perform miniemulsion ATRP was assessed.[18] After its addition to a miniemulsion made of MMA droplets containing an alkyl halide, **GC1-PEO** migrates progressively through the dispersing phase and, due to its amphiphilic nature, penetrates into the droplets and promotes the ATRP of MMA. The polymerization led to almost complete conversions with fast kinetics (compared with solution conditions). Besides, a relatively fair correspondence (initiation efficiency $f \approx 0.8$) between the targeted and obtained molar masses and molar mass distributions slightly broader than those obtained in solution were achieved with increased amounts of **GC1-PEO**. With lower amounts, the initiation efficiency was indeed lower and the polymer dispersity higher, indicating that a partial loss of control occurred.

Finally, ROMP and ATRP were combined simultaneously for the preparation of

Table 1.
The results obtained for the different polymerizations performed under miniemulsion conditions.

Entry	Description	Polymer-type	Conversion^1		$M_{n,exp}^2$	M_w/M_n^2	d_d^3	d_p^3
	molar ratios		NB	MMA	($g \cdot mol^{-1}$)		(nm)	(nm)
1	**[NB]/[Ru]** 1400/1	PNB	97%	–	67000*	2.2	234	211
2	**[MMA]/[ini-Cl]/[Ru]** 513/1/0.77	PMMA	–	94%	46700	1.8	191	198
3	**[NB]/[MMA]/[ini-Cl]/[Ru]** 225/214/1/0.4	*PNB* *PMMA*	100%	97%	*problematic fractionation of the products*		207	184
4	**[NB]/[MMA]/[I1]/[Ru]** 14/24/1/0.03	PNB-*g*-PMMA	100%	97%			216	187
5	**[NB]/[MMA]/[I1]/[Ru]** 6/25/1/0.03	PNB-*g*-PMMA	99%	97%			235	232

Conditions: nitrogen atmosphere, $T = 60$ °C, 6 h. ATRP initiator: ini-Cl = ethyl 2-chloropropanoate.
[1] Monomers conversions determined by Gas chromatography.
[2] Number-average molar mass and polymer dispersity determined by SEC.
Calibration with PMMA standards for PMMA and PS standards for PNB.
[3] Z-average droplet (d_d) and particle (d_p) hydrodynamic diameters as measured by DLS.
*This value is only an approximation (due to the presence of unreacted **GC1-PEO** and calibration with PS standards).



Scheme 2.

Structures of the alkylideneruthenium used in this study both as ROMP initiators and ATRP catalysts. (**GC1**) first-generation Grubbs catalyst. (**GC1-PEO**) water-soluble macrocatalyst (here: $a \approx 100$ and $b \approx 3$). The second polymerization degree "b" is targeted stoichiometrically. Owing to its small value and to the steric hindrance of the PEO macromonomers, the number of inserted PEO grafts may differ from one macrocatalyst molecule to another.

homopolymer blends and graft-copolymers.[18] The use of **GC1-PEO** led to almost complete conversions of both monomers. Because of complexity of the system, attempts to separation of different components of the products (polymers, surfactant, residual **GC1-PEO**) by means of selective precipitation in ethanol and acetone were not successful. However, the SEC traces corroborated the formation of two polymers for the tandem homopolymerizations and only a single peak (plus the peak corresponding to the surfactant) was observed when graft-copolymers were targeted.

From a colloidal point of view, all miniemulsion polymerizations described in this study gave rise to well-defined particles with fair size distributions and average hydrodynamic diameters of about 200 nm. In addition, particle morphologies were further investigated combining transmission electron microscopy (TEM) and atomic force microscopy (AFM, tapping-mode), as displayed in Figure 1. Whereas PNB particles *(entry 1, Table 1, Fig. 1A)* could directly be observed by TEM, negative staining using uranyl acetate was required to reveal PMMA particles *(entry 2, Fig. 1B)*. Concerning the latices made of a 50/50 blend of both homopolymers *(entry 3, Figs. 1C, 1C' and 1C'')*, most of the particles adopt hemispherical morphology made of a PMMA phase (light on TEM images) partially engulfed in a PNB shell (dark). Besides, in AFM images, some of these particles exhibited a large cavity which tended to indicate that the PMMA phase can be expulsed from the PNB shell. This result was confirmed by TEM, using staining with ammonium molybdate that deposited between the particles and inside some PNB shell, indicating that only a part of PNB shells were really empty. When graft-copolymer particles were considered, the morphology was considerably affected by the supplementary constraints due to the linkage of incompatible polymer chains in the same macromolecule PMMA side-chains connected to a PNB backbone. TEM and AFM *(entry 5, Figs. 1D and 1D')* clearly displayed occluded structures made of dark particles (PNB-rich phase, portions of the backbone) with external and possibly internal light occlusions (PMMA-rich phase: local gathering of PMMA grafts).

Second Route: Simultaneous ROMP and ATRP from Two Distinct Microemulsions

Despite its very high efficiency, the previous miniemulsion route presents a rele-

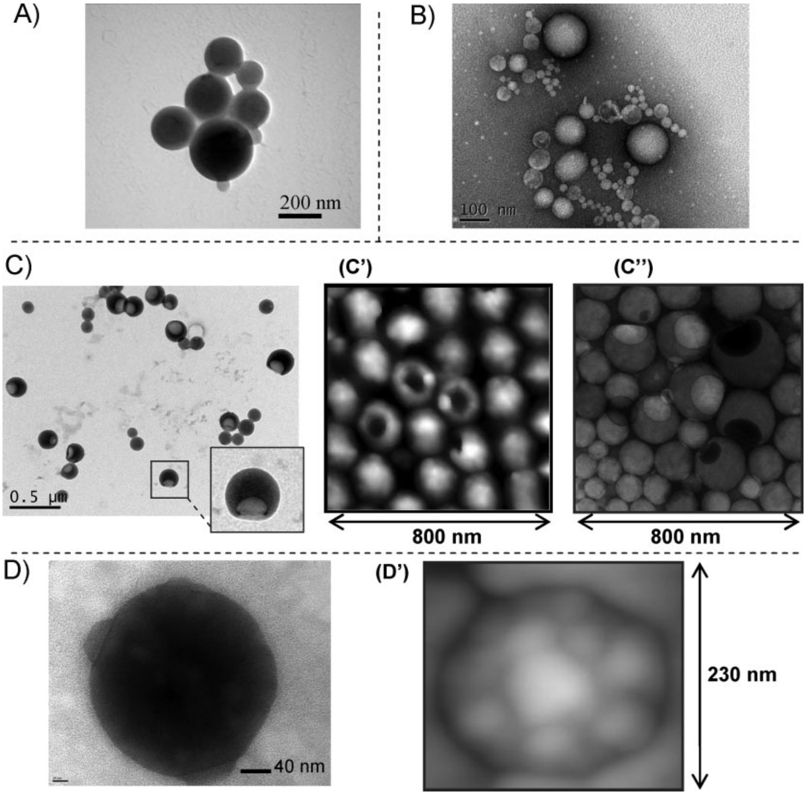


Figure 1.
Imaging of the latices prepared by miniemulsion polymerization. **PNB:** ***entry 1 of Table 1*** **(A)** TEM, without staining. **PMMA:** ***entry 2 of Table 1*** **(B)** TEM, staining with uranyl acetate. **PNB/PMMA:** ***entry 3 of Table 1*** **(C)** TEM, staining with uranyl acetate, **(C')** AFM height image, **(C'')** TEM, staining with ammonium molybdate. **PNB-*g*-PMMA:** ***entry 5 of Table 1*** **(D)** TEM, staining with ammonium molybdate, **(D')** AFM height image.

vant drawback: the modification of **GC1** towards water-solubility is a time-consuming and very delicate synthesis. Moreover, the PEO chains inserted into the catalyst remain in the final structure (unavoidable functionalization of one of the PNB chain ends). So as to get rid of this issue, we later proposed to use directly the commercial hydrophobic shape of **GC1** using a new alternative[19] inspired by the work of Mecking and coworkers on microemulsion ROMP.[20,21] The approach is based on the use of two aqueous microemulsions: the first one has a dispersed phase composed of the monomers (NB, MMA and Ethyl 2-chloropropionate or **I1**) whereas the droplets of the second one contain **GC1** solubilised in toluene. Once they have been mixed together, thermodynamically driven exchanges between the droplets of both microemulsions enable **GC1** to meet the other reagents and thus to trigger off the ROMP of NB and the ATRP of MMA.

Table 2 summarizes some tests performed following this approach for the synthesis of homopolymer binary blend particles and graft-copolymer particles. The particle yields and overall conversions given for each situation were measured gravimetrically and correspond to overall values: no piece of information is given about the conversion of each monomer *(for entries 3–5)*. Thus, the prepared polymers were analyzed quantitatively by ^{1}H NMR.

Table 2.
The results obtained for the different single-catalyst polymerizations performed using two distinct micro-emulsions.

Entry	Description	Polymer-type	$M^1_{n,exp}$	M_w/M^1_n	d^2_p	Coagulation^3	OC^4	f^5
	molar ratios		(g · mol^{-1})		(nm)			
1	**[NB]/[Ru]** 782/1	PNB	99500	1.5	21	8%	66%	1.1
2	**[MMA]/[ini-Cl]/[Ru]** 765/2.3/1	PMMA	97200	1.6	37	0	79%	0.2
3	**[NB]/[MMA]/[ini-Cl]/[Ru]**	*PNB*	*63700*	*1.9*	46	5%	60%*	*0.8***
	388/400/2.3/1	*PMMA*	*81800*	*2.1*				*0.1***
4	**[NB]/[I1]/[MMA]/[Ru]** 194/30/533/1	PNB-*g*-PMMA	66400	2.0	44	2%	61%*	–
5	**[NB]/[I1]/[MMA]/[Ru]** 388/30/365/1	PNB-*g*-PMMA	104600	1.8	49	4%	69%*	–

Conditions: nitrogen atmosphere, $T = 60$ °C, 8 h.
ATRP initiator: ini-Cl = ethyl 2-chloropropanoate.
[1] Number-average molar mass and polymer dispersity determined by SEC.
Calibration with PS standards.
[2] Z-average particle hydrodynamic diameter as measured by DLS.
[3] Extent of coagulation: $m_{\text{coagulates}}/m_{\text{monomer}}$.
[4] OC: Overall conversion $= (m_{\text{polymer from particles}} + m_{\text{polymer from washed coagulates}})/m_{\text{monomer t}=0}$.
[5] Initiation efficiency factor: $f = \frac{\overline{M}_n^{th}}{\overline{M}_n^{exp,corr}}$ with $\overline{M}_n^{th} = \frac{[monomer]_0}{[initiator]_0} \times M_{monomer} \times conversion$ and $\overline{M}_n^{exp,corr} = \alpha \times \overline{M}_n^{exp}$ ($\alpha = 1.28$ for PMMAand 0.45 for PNB).[22]
*particle yields and overall conversions are estimation of the conversion of all monomers: entry 3: NB + MMA, entries 4 and 5: I1 + NB + MMA.
**For entry 3, f values have been estimated using the polymer mixture composition determined from NMR.

For entries 3–5, the accordance of the obtained values with the initial ratio of the monomer mixture indicated conservation of the composition of the polymer. The latter result may be related to the “relatively close” overall conversions ($m_{\text{polymer}}/m_{\text{monomers}} + m_{\text{coagulate}}/m_{\text{monomer}}$: 66% for ROMP versus 79% for ATRP) obtained after 8 h at 60 °C for the ROMP of NB and the ATRP of MMA, when carried out separately. In fact, this tends to indicate that the tandem fashion has no relevant influence on the conversions of each polymerization, and confirms the suitability of **GC1** as tandem catalyst in our conditions.

Whatever were the experimental conditions (ROMP alone, ATRP alone, simultaneous homopolymerizations, or preparation of copolymers), the overall monomer conversions were incomplete (between 60 and 79%). These values measured gravimetrically may be underestimated. Nevertheless, the particular thermodynamic order created under microemulsion conditions may cause limitations for monomer diffusion.

Furthermore, a good correspondence between the experimental and the theoretical molar masses was obtained for the ROMP of NB, when performed alone or in the frame of simultaneous polymerizations *(entries 1 and 3)*. This was not the case for the ATRP of MMA which yielded chains of high molar masses *(entries 2 and 3)*. Not surprisingly, the initial separation of the catalyst and the thermodynamically driven exchanges between the droplets of both microemulsions are not the most favourable case to perform ATRP, but it allows its combination with ROMP. However, for both polymerizations, the polydispersities of the synthesized polymers were fair and corresponded to the values obtained for related solution conditions.[18] In addition, the increase in the polydispersities observed for simultaneous polymerizations tended to indicate a slight perturbation of the activity of **GC1** both as ROMP initiator and as ATRP catalyst under these conditions.

When applied to the preparation of graft-copolymer made of a PNB backbone and PMMA side-chains, the route led to slightly broader molar mass distributions (between 1.8 and 2.0). To check that the prepared polymers are effectively grafted structures, their NMR spectra were qualitatively scrutinized. In all cases, peaks corresponding to PMMA were obviously observed ($\delta_{-CH3} = 0.7–1.1$ ppm, $\delta_{-CH2-} = 1.7–2$ ppm and $\delta_{-OCH3} = 3.6$ ppm). However, the non-appearance of remaining NB cyclic double bonds ($\delta_{C=C} = 5.9–6.2$ ppm) was a proof for the absence of parasite homo-PMMA (**I1** was the single component capable of initiating ATRP). Even if the peaks corresponding to the PNB backbone were easily identified ($\delta_{C=C} = 5.2–5.4$ ppm), no piece of information was available on the possible presence of homo-PNB. Nevertheless, only one well-defined peak was displayed on SEC traces.

Concerning the colloidal aspect of the prepared latices, DLS analysis revealed narrow size distributions and z-average hydrodynamic diameters smaller than 50 nm. Hence, the suitability of the approach is confirmed from the colloidal point of view. Furthermore, a limited coagulation ($\leq 8\%$) occurred when NB

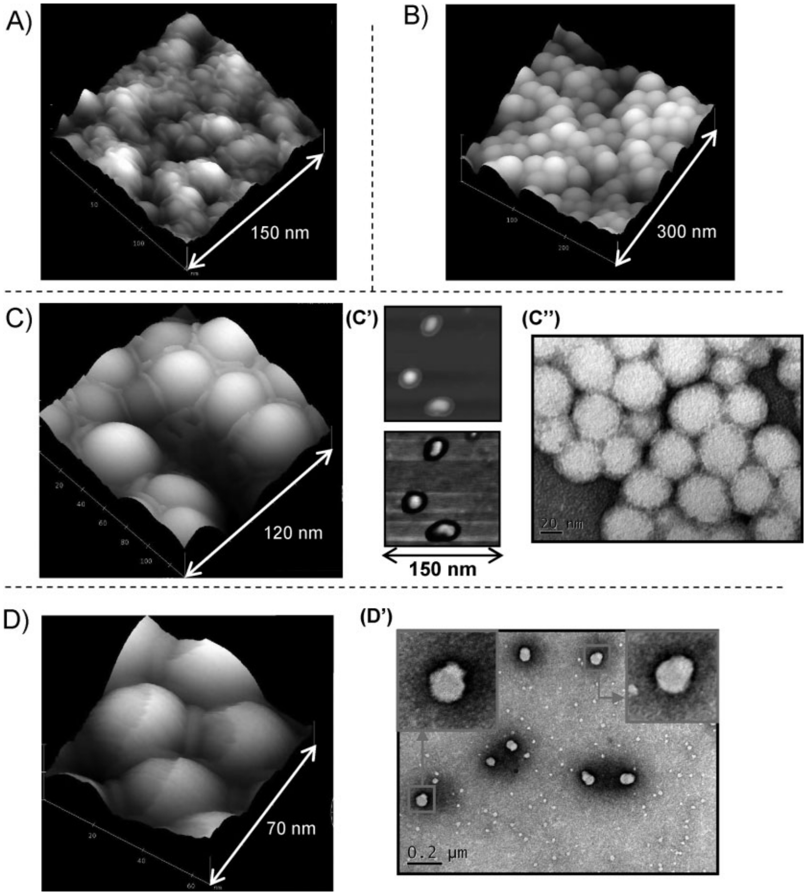


Figure 2.
Imaging of the nanoparticles prepared under microemulsion conditions. **PNB:** ***entry 1 of Table 2*** **(A)** AFM height picture. **PMMA:** ***entry 2 of Table 2*** **(B)** AFM height picture. **PNB/PMMA:** ***entry 3 of Table 2*** **(C)** AFM height picture, **(C')** *after dilution of the latex,* two-dimensional AFM height (top) and phase (bottom) pictures, **(C'')** TEM picture, staining with uranyl acetate. **PNB-*g*-PMMA:** ***entry 5 of Table 2*** **(D)** AFM height picture, **(D')** TEM picture, staining with uranyl acetate.

was involved in the reaction and tended to increase as the ratio of this monomer was raised. The nanoparticles were finally imaged by AFM and TEM. Depending on the particle constituents, different morphologies were obtained (Figure 2). The particles composed of a single polymer were first examined. Despite the incomplete conversions, PMMA particles displayed relatively sharp contour whereas PNB particles tended to crush in the contact areas. For PNB/PMMA homopolymer blend particles *(entry 3 of Table 2, Figs. 2C, 2C' and 2C'')*, dilutions were carried out in order to isolate individual particles. AFM exhibited a relatively ''hard'' core – surely PMMA - surrounded by a softer material, certainly PNB. Nevertheless, TEM pictures displayed ''common'' spherical shapes. Hence, before being deposited, the particles had probably a core-shell or hemispherical structure (with an almost complete engulfment of the core). For PNB-*g*-PMMA particles *(entry 4 of Table 2, Figs. 2D and 2D')*, ''acorn-like'' (also referred to as ''hemispherical'') morphologies were observed. The phase images (*not shown here*) indicated that the shell was softer than the contained phase. In contrary to homopolymer blend particles, no spreading of the soft shell was observed. These original morphologies are currently further examined.

Conclusion

The results of the two approaches presented in this article emphasize the interesting features and the straightforwardness of a simultaneous combination of ROMP and ATRP in dispersed media for preparation of polymer composite particles. Even if the approaches are based on the same strategy, their mechanistic differences allow to reach different size rangeon one hand and to obtain different morphologies on the other. Owing to specific pros and cons of each approach, it would be more suitable to consider them complementarily than trying to find the best one. Concerning the current perspectives of this work, extending the routes to other monomers and understanding and controlling the particle morphology are of primary interest.

[1] B. Schuler, R. Baumstark, S. Kirsch, A. Pfau, M. Sandor, A. Zosel, *Prog. Org. Coat.* **2000**, *40*, 139–150.

[2] P. A. Lovell, D. Pierre, *Emulsion polymerization and emulsion polymers*, John Wiley and Sons, New York **1997**, pp. 657–695.

[3] Y. C. Chen, V. Dimonie, M. S. El-Aasser, *Macromolecules* **1991**, *24*, 3779–3787.

[4] M. Okubo, R. Takekoh, N. Saito, *Colloid Polym. Sci.* **2003**, *281*, 945–950.

[5] A. Koenig, U. Ziener, A. Schaz, K. Landfester, *Macromol. Chem. Phys.* **2007**, *208*, 155–163.

[6] T. Kietzke, D. Neher, M. Kumke, O. Ghazy, U. Ziener, K. Landfester, *Small* **2007**, *3*, 1041–1048.

[7] J. Nicolas, A.-V. Ruzette, C. Farcet, P. Gérard, S. Magnet, B. Charleux, *Polymer* **2007**, *48*(24), 7029–7040.

[8] N. Saito, Y. Kagari, M. Okubo, *Langmuir* **2007**, *23*, 5914–5919.

[9] T. Fujibayashi, M. Okubo, *Langmuir* **2007**, *23*, 7958–7962.

[10] C. W. Bielawski, J. Louie, R. H. Grubbs, *J. Am. Chem. Soc.* **2000**, *122*, 12872–12873.

[11] R. Charvet, B. M. Novak, *Macromolecules* **2004**, *37*, 8808–8811.

[12] C. Cheng, E. Khoshdel, K. L. Wooley, *Nano Lett.* **2006**, *6*, 1741–1746.

[13] J. Qiu, B. Charleux, K. Matyjaszewski, *Prog. Polym. Sci.* **2001**, *26*, 2083–2134.

[14] K. Min, H. Gao, K. Matyjaszewski, *J. Am. Chem. Soc.* **2005**, *127*, 3825–3830.

[15] M. F. Cunningham, *Prog. Polym. Sci.* **2008**, *33*, 365–398.

[16] D. Quémener, V. Héroguez, Y. Gnanou, *Macromolecules* **2005**, *38*, 7977–7982.

[17] D. Quémener, V. Héroguez, Y. Gnanou, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2784–2793.

[18] C. Airaud, V. Héroguez, Y. Gnanou, *Macromolecules* **2008**, *41*, 3015–3022.

[19] C. Airaud, E. Ibarboure, C. Gaillard, V. Héroguez, submitted.

[20] V. Monteil, P. Wehrmann, S. Mecking, *J. Am. Chem. Soc.* **2005**, *127*, 14568–14569.

[21] S. Mecking, V. Monteil, J. Huber, L. Kolb, P. Wehrmann, *Macromol. Symp.* **2006**, *236*, 117–123.

[22] These factors correspond to experimental corrections. They aim at approximating the ''real'' values of the average molar masses from the ''apparent'' ones measured by SEC. For PMMA, the value has been determined using PMMA standards. For PNB, it has been taken from the following reference: V. Héroguez, M. Fontanille, *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1755–1760.