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Polynorbornene latex synthesis by UV-triggered Ring-Opening Metathesis Polymerization in Miniemulsion

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ABSTRACT

An innovative route based on a novel photo-latent ROMP initiator has been explored to synthesize polynorbornene latex particles in miniemulsion. Operation conditions were strongly improved by the use of an annular LED photo-reactor, increasing the uniformity of radiation distribution and enabling to control atmosphere and stirring throughout irradiation. Several parameters (droplet size, irradiance, pre-catalyst structure) were studied in order to improve the monomer conversion profiles, which eventually led to the

production of latex with high norbornene conversion (> 90 %) and 10 % solids content. Particular attention was paid to the polymer microstructure, which was found to be highly dependent on the type of initiation mechanism.

Keywords: Photo-latent initiator, Ring-Opening Metathesis Polymerization, polymerization in miniemulsion, latex

1- Introduction

Aqueous miniemulsion polymerization is a powerful process to obtain polymer latex from highly hydrophobic monomers since every droplet acts as a nanoreactor in theory. Thanks to the tolerance of radicals towards water, free radical polymerization has been the most employed reaction to polymerize a monomer miniemulsion. This is usually achieved by heating a hydrophobic thermal radical initiator dissolved in the emulsified organic phase.[1-4] In order to expand the range of latexes available, the use of other polymerization processes including Ring-Opening Metathesis Polymerization (ROMP) is highly desirable. Aqueous dispersions based on polyunsaturated ROMP polymers like polynorbornene (PNb) hold potential to create a new class of dispersed materials having high mechanical strength or polymer microstructures which cannot be prepared by conventional free-radical polymerization. Nevertheless, this field is still poorly documented because of both the water sensitivity of most ROMP catalysts and their absence of latency resulting in premature polymerization.[5] Today, miniemulsion polymerization has proven to be one of the most suitable processes for developing ROMP in dispersed systems.

The first successful miniemulsion ROMP was accomplished by Claverie *et al.* in 2001[6] through the dropwise addition of the cyclo-olefin monomers into a catalyst miniemulsion in order to address the issue of premature polymerization. However, only the least reactive monomers (cyclooctene, cyclooctadiene) could be polymerized without signs of destabilization. Five years later, our group described the miniemulsion ROMP of strained monomers by adding a water-soluble macroinitiator to a monomer miniemulsion.[7] The same strategy was used to successfully perform a tandem combination of ROMP and Atom Transfer Radical Polymerization (ATRP) in miniemulsion.[8,9] The drawback of this approach is the challenging synthesis of the macro-initiator. A similar approach was recently employed by Cunningham *et al.*[10] through the design of a triethylene glycol-functionalyzed Ru-based catalyst able to undergo phase transfer from the aqueous phase to the monomer droplets once activated. To overcome the issue of uncontrollable polymerization, a more efficient strategy could be the use of latent catalysts complexes.[11-15] By being able to release active species *in situ* and "on demand" after external stimulation, such catalyst could greatly simplify the conditions for the implementation of ROMP in miniemulsion.

In a previous contribution, we described an efficient photo-latent ROMP initiator resulting from the photogeneration at 365 nm of the 1,3-dimesitylimidazol-2-ylidene (IMes) N-heterocyclic carbene (NHC).[16-17] Subsequent reaction with the inactive ruthenium dimer $[RuX_2(p\text{-cymene})]_2$ (X=Cl or I) led to the *in situ* formation of the Noels' catalyst $X_2Ru(p\text{-cymene})(IMes)$ (X=Cl or I) able to initiate the ROMP of Nb in solution (supplementary information, Scheme S1).[18] Furthermore, we showed that such photolatent system was also able to trigger the photoROMP of Nb in miniemulsion.[19] However, only 40 % conversion were achieved whatever the

experimental conditions used. In addition, only small amounts of polymer were produced (less than 10 mg) thus limiting industrial recovery and extensive characterization of the produced polymer.

In these initial trials, photopolymerization was carried out in a very basic and not scalable reaction vessel (quartz cuvette with low optical path), implying major drawbacks such as low polymer yield, significant losses of incident radiation and fluctuating irradiance values.

Given this context, the process is likely to be significantly improved by the use of a well designed photochemical reactor able to optimize incident radiation, improve conversion per unit of times and increase the uniformity of radiation distribution. Such process improvement's approach relying on photochemical technology has already demonstrated its efficiency and added value in areas such as preparative organic photochemistry, water disinfection, and oxidative treatment of air.[20] In polymer chemistry, a large scale use of photoreactors has not yet taken place. However, complex polymerization processes such as photoROMP could benefit from photochemical engineering development. In this contribution, a commercial immersion-type photoreactor of 150 mL has been selected, that is equipped with a monochromatic high powered LED light source (365 nm) (Figure 1). This radiation source is contained in a double-jacketed water-cooled well that is itself immersed into a stirred reaction system. The advantage is that the emitted radiation is entirely incident to the photochemically reactive system, with no loss of radiation.

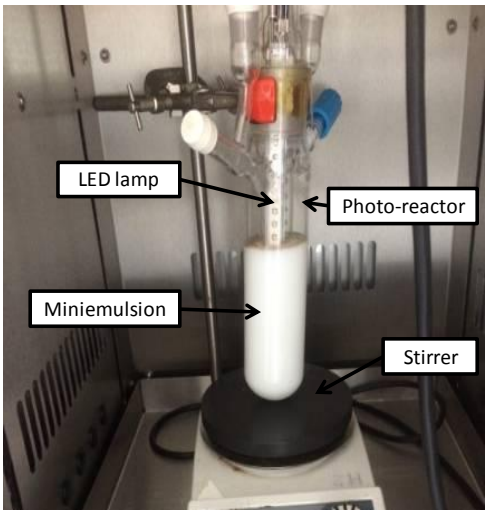


Figure 1: Picture of the annular photo-reactor

In this report, we employed this annular photoreactor for the photo-latent ROMP of Nb in miniemulsion in the presence of the three component system: $IMesH^+BPh_4^-$ /ITX/$[RuX_2(p\text{-cymene})]_2$. In a first part, the efficiency of this new photochemical reactor was evaluated as regards reaction kinetics, polymer molecular weight and dispersity. Then, particular attention was paid to the effects of the polymerization parameters on the conversion kinetic profiles and on the characteristics of the polymers formed.

2- Experimental part

2.1- Materials:

Ethanol (EtOH; 96 %), chloroform ($CHCl_3$; 99.4 %), dichloromethane (DCM; 99.8 %) from VWR Chemicals and 1,2-dichloroethane (DCE; 99.8 %) from Aldrich were used without further purification. 1,3-dimesitylimidazolium chloride ($IMesH^+Cl^-$; 97 %) and sodium tetraphenylborate ($NaBPh_4$; 99.5 %) were purchased from ABCR. Dichloro(*p*-cymene)ruthenium(II) dimer ($[RuCl_2(p\text{Cy})]_2$; 98 %) and diiodo(*p*-cymene)ruthenium(II) dimer ($[RuI_2(p\text{Cy})]_2$) were purchased from Alfa Aesar. 2-isopropylthioxanthone (ITX; 98 %) was

obtained from TCI Europe. Brij®S100 (steric surfactant), norbornene (Nb) and hexadecane were purchased from Aldrich. Deionized water was obtained with a Millipore Milli-Q Biocel A10 purification unit. 1,3-dimesitylimidazolium tetraphenylborate ($IMesH^+BPh_4^-$) was obtained as described in previous article.[18]

2.2- Irradiation source:

Miniemulsion irradiations were performed in an annular regular glass reactor[21] thanks to a LED lamp novaLIGHT TLED 100-365 from Peschl Ultraviolet at 365 nm. Irradiance was measured with a Power Puck II radiometer from EIT®. The optical path length was 8 mm.

2.3- Nb miniemulsion ROMP:

In this study, all the miniemulsions were performed in a photo-reactor equipped with an airtight sonication probe and prepared with a dispersed phase content of 10 w/w % following a process similar to that previously described[19] (see Supporting Information for more details).

2.4- Characterization methods:

^{1}H NMR spectra were acquired on samples precipitated in acetone, using a Bruker spectrometer 400 MHz employing $CDCl_3$ or DMSO-d_6 as solvent at 25 °C. Conversion of Nb was determined by GC with hexadecane as internal standard, using a VARIAN GC3900 (apolar capillary column BP1-30m; injector temperature: 250 °C; detector temperature: 300 °C; ramp temperature: 2 min at 50 °C + 10 °C/min until 250 °C; GC retention times: t^{GC}_{Nb} = 1.77 min; $t^{GC}_{dodecane}$ = 13.25 min). Dynamic light scattering

(DLS) measurements were performed using a MALVERN Zetasizer Nano ZS equipped with He-Ne laser (4 mW; 633 nm). All size distributions are the average of three measurements. Before measurements, latexes were diluted about 250 times to minimize multiple scatterings caused by high concentration. The scattering angle used was 90 °. Size-exclusion chromatography (SEC) was performed on samples precipitated in acetone, in tetrahydrofuran (THF) (1 $mL.min^{-1}$) with trichlorobenzene as the flow marker, using both refractometric and UV detectors. TEM pictures were performed with a HITACHI H7650 microscope operating at an accelerating voltage of 80 kV. Latexes were diluted 70 times and 10 µL of the final latexes were poured on carbon-carbon grids and dried in normal atmosphere. The pictures were recorded with Digital Micrograph (GATAN) and analyzed with the software ImageJ to determine the particle average diameter and the polydispersity (PDI). PDI is calculated with the following formula (Equation 1):

$$PDI = \left(\frac{\sigma}{D}\right)^2 \quad \text{Equation 1}$$

With:

D: the average diameter, σ: the standard deviation.

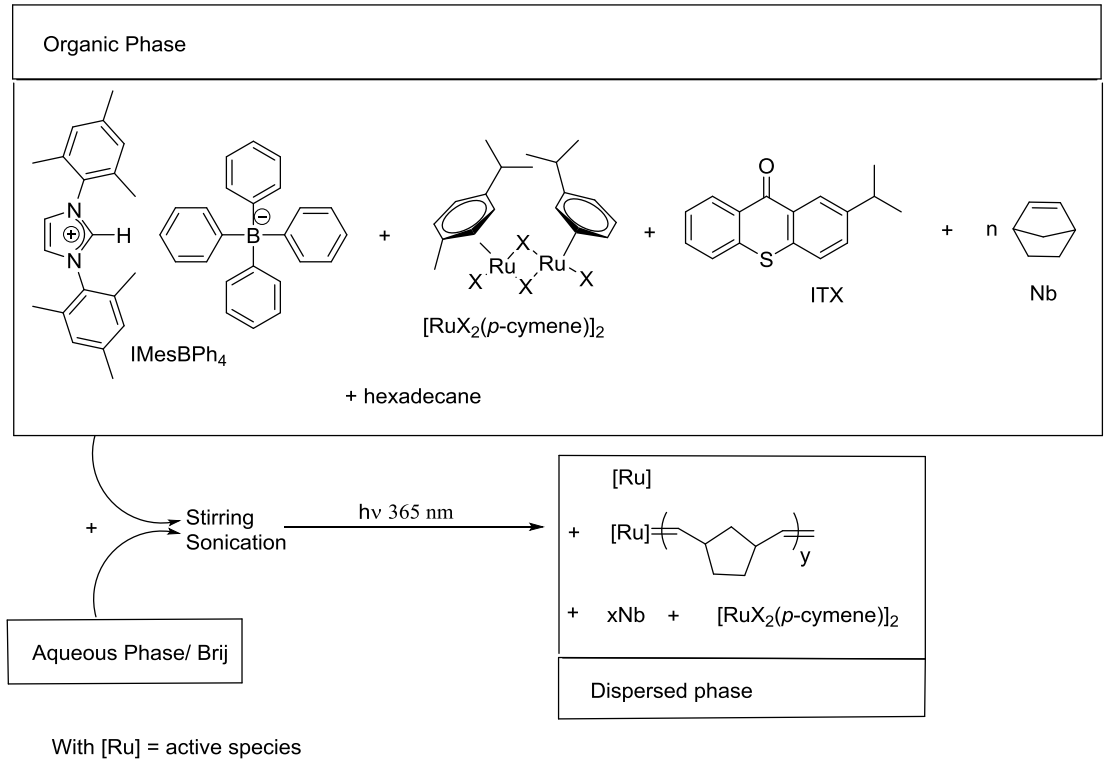
3- Results and discussion

150 mL of Nb miniemulsion (10 % solids content) was placed in the annular regular glass photochemical reactor under well-controlled inert atmosphere (Figure 1). Aliquots were regularly withdrawn during the photoROMP progress to perform a range of polymer characterizations impossible with the previous closed setup.

3.1- Miniemulsion ROMP in annular reactor:

A Nb miniemulsion was prepared after 2 min sonication time using $IMesH^{+}BPh_4^{-}$ /ITX/[$RuCl_2$(*p*Cy)] (5/2.5/1 equiv.) as ROMP photocatalytic system. The ROMP was triggered by subjecting the dispersed medium to irradiation for 5 to 60 min at 365 nm at 130 mW/cm² (Scheme 1). Nb conversion reached only 36 % after 60 min (Figure 2 blue curve) which is comparable to the conversion obtained in the previous study.[19]

Scheme 1: Formation of PNb latex



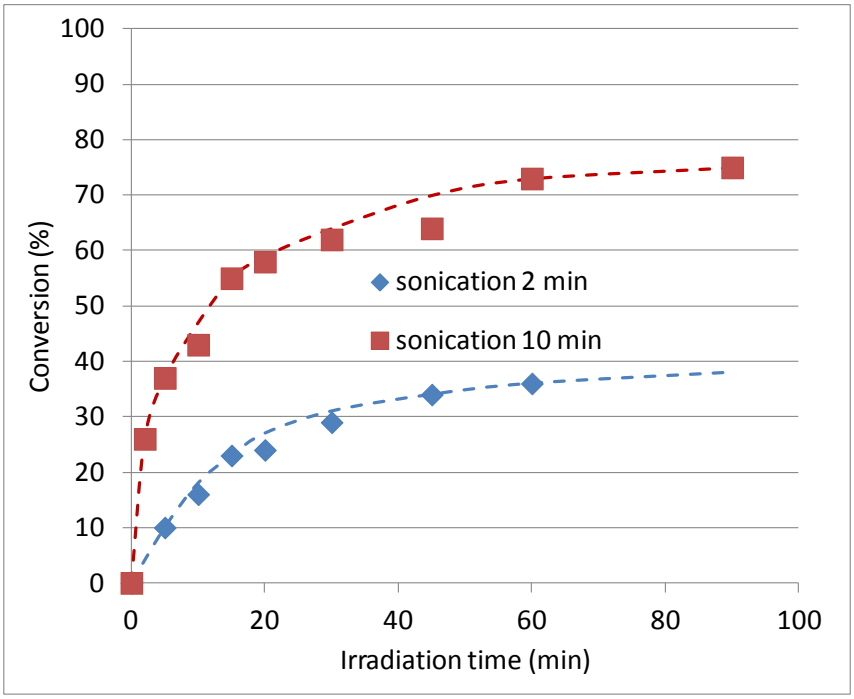


Figure 2: Nb conversion as a function of the irradiation time for the miniemulsion ROMP with the catalytic system $IMes^{+}BPh_4^{-}$/ITX/$[RuCl_2(pCy)]_2$ (5/2.5/1 equiv.); irradiance 130 mW/cm²; in blue after 2 min of sonication and after 10 min of sonication in red.

One of the reasons for this low conversion value could be the large increase of irradiated volume (150 ml in annular reactor versus 0.3 ml in quartz cell) thus decreasing the overall amount of incident photons to unit volume of emulsion. But another reason can be found in the droplet and particle sizes formed during this experiment. Indeed, the DLS analysis after 60 min of irradiation shows latex particles size of 156 nm (PDI = 0.092), close to the droplet size of the miniemulsion (138 nm, PDI = 0.134) (Figure 3), which is much larger than the size of droplets and particles prepared in our previous experiment (of about 100 nm). This relatively high value of the droplets size, resulting in scattering and thus low penetration of the light, coupled with a high optical path length (8 mm) could explain the limited Nb conversion. To

tackle this problem, the miniemulsions were sonicated for 10 min instead of 2 min, resulting in much smaller droplets with average diameter of 92 nm (PDI = 0.181) (Figure 3). After 60 min of irradiation, the latex derived from this smaller miniemulsion exhibited much higher Nb conversion of 75 % (Figure 2 red curve). Additionally, the final particles have sizes close to the initial droplets size of the miniemulsion (101 nm (PDI = 0.118) Figure 3). TEM characterization of the final particles shows spherical particles with sizes consistent with the values measured by DLS data (95 nm (PDI = 0.067)) (Figure 3).

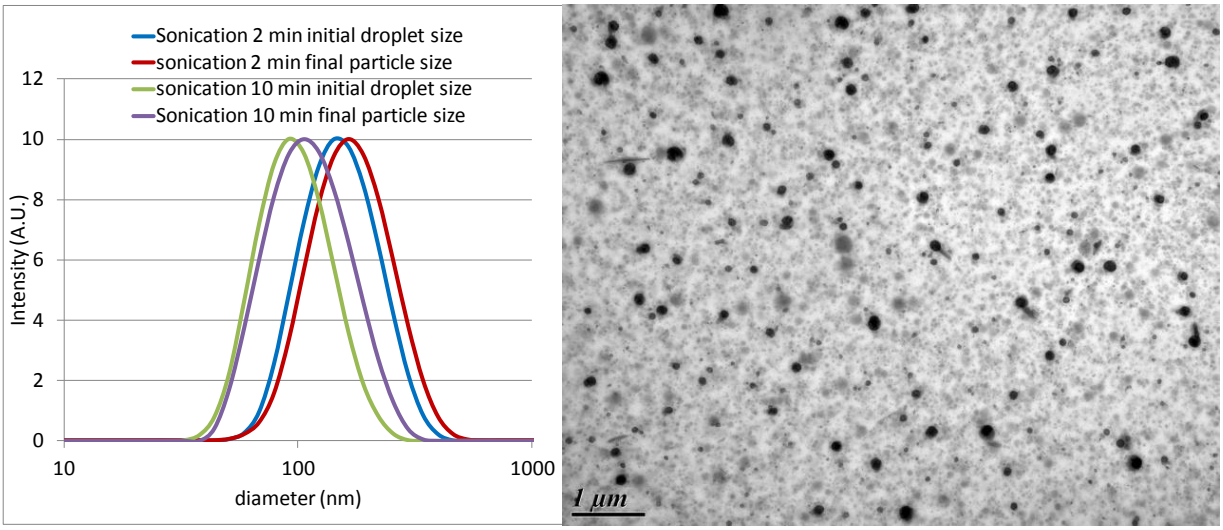


Figure 3: Left: initial droplet size and final particle size measured by DLS for the miniemulsion ROMP with the catalytic system $IMes^{+}BPh_4^{-}$/ITX/$[RuCl_2(p\text{Cy})]_2$ (5/2.5/1 equiv.); irradiance 130 mW/cm² for 2 min and 10 min of sonication. Right: TEM picture of the final particles for a sonication time of 10 min.

In order to gain a deeper insight into the polymerization mechanism occurring during the irradiation, aliquots were withdrawn from the reaction media at regular time intervals. For each sample, a small portion was analyzed by GC to determine Nb conversion while the remaining part was precipitated in acetone for ^{1}H NMR and SEC

analyses (Table 1). For all polymer samples, experimental average molar masses were much higher than the theoretical ones, indicating a poor initiation efficiency of the polymerization. The latter can be due to low efficiency of catalyst formation, slow initiation or partial degradation of catalyst under irradiation. However, the poor stability of the Noel's catalyst does not allow us to prove one or the other of these hypotheses. The polymers also exhibited broad molecular weight dispersities around Đ = 2 (supplementary information Figure S1). Regarding the ^{1}H NMR spectra, characteristic signals of PNb are detected with suitable integrations, particularly the signals corresponding to the unsaturations of the PNb chains (δ = 5.35 and 5.21 ppm) (supplementary information Figure S2). The cis/trans ratios of the obtained polymers are about 60/40 and do not vary with the irradiation time and thus with the conversion.

ROMP in dichloromethane solution under the same conditions (130 mW/cm² during 60 min) was also performed in order to compare the solution and miniemulsion photopolymerizations. Lower conversions (50 %) were achieved in solution versus 75% in miniemulsion (supplementary information Figure S3). In the case of solution polymerization, a high increase of the viscosity of the reaction medium was observed. Furthermore, the precipitation of the formed polymer and its deposition on the reactor wall caused a significant irradiation shielding. In contrast, these drawbacks were not found in miniemulsion polymerization where the viscosity of the reaction medium remained low and no fouling was observed on the wall of the photoreactor. Consequently, miniemulsion ROMP offered very interesting benefits compared to solution ROMP. In the rest of this contribution, the influence of several parameters on

the monomer conversion profiles and the characteristics of the obtained polymers in miniemulsion have been studied.

Table 1: Characteristics of the obtained polymers with the catalytic system $IMesH^+BPh_4^-$ /ITX/$[RuCl_2(pCy)]_2$ (5/2.5/1 equiv.) for the polymerization in miniemulsion. Sonication time 10 min, irradiance 130 mW/cm².

Irradiation time (min)	2	5	10	15	20	30	45	60	90
Nb conversion (%)	26	37	43	55	58	62	64	73	75
$M_{n;th}$ (kg/mol)*	25	35	41	53	56	59	61	70	72
$M_{n;expcor}$ (kg/mol)**	248	250	186	249	149	155	140	128	135
Đ	2.04	2.03	2.59	1.85	2.97	2.78	3.43	3.25	2.79
$\%_{cis}$***	-	-	-	61	60	61	62	62	63

* $M_{n;th}=(\pi_{Nb}\times M_{Nb}\times n_{Nb})/(2\times n_{[RuCl2(pCy)]2})$ where π_{Nb} is the Nb conversion, M_{Nb} is the molecular weight of Nb, n_{Nb} is the initial amount of Nb, $n_{[RuCl2(p\text{-}cymene)]2}$ is the initial amount of $[RuCl_2(pCy)]_2$

** Determined by SEC (PS eq.) and corrected: $M_{real}=M_{n;expcor}=M_{measured}/2$

*** $\%_{cis}=I_{cis}/(I_{cis}+I_{trans})$ where I_{cis} is the integration on the ^{1}H NMR spectrum of the signal corresponding to the protons of the *cis* double bonds at 5.21 ppm and I_{trans} is the integration of the signal of the protons of the *trans* double bonds at 5.35 ppm

3.2- Influence of irradiance:

In the previous experiments, the irradiation was carried out at 130 mW/cm². This high level of irradiance can cause side reactions including adventitious initiation by $[RuCl_2(pCy)]_2$ (without NHC), but also polymer chains or catalyst degradation reactions. Consequently, our attention has been focused on the influence of irradiance on Nb conversion profile (Figure 4 blue curve) and on the characteristics of the formed polymer. At 25 mW/cm², high conversions were achieved at much higher rates (more than 75 % after 30 min of irradiation) and an almost complete monomer conversion was obtained after 90 min of irradiation. The stability of the miniemulsion

during the ROMP was also preserved as attested by good correspondence between droplet size (96 nm (DPI = 0.178) and final particle size (98 nm (DPI = 0.156). The chemical characteristics of the formed polymers are presented in Table 2.

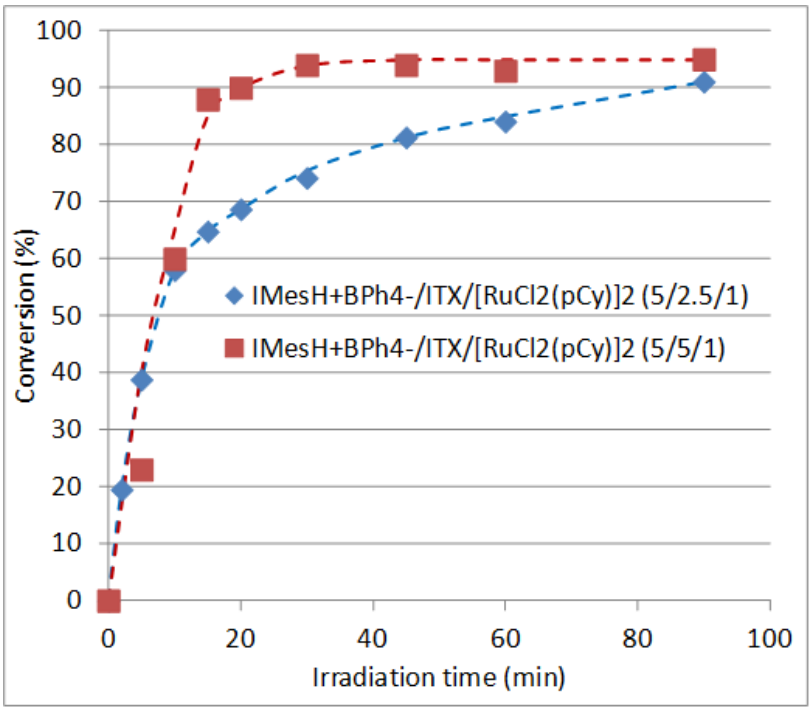


Figure 4: Nb conversion as a function of the irradiation time for the miniemulsion ROMP with the catalytic system $IMes^{+}BPh_4^{-}$/ITX/$[RuCl_2(pCy)]_2$ (5/2.5/1 equiv.) blue curve and (5/5/1 equiv.) red curve; irradiance 25 mW/cm²; sonication time 10 min.

Regarding the ^{1}H NMR spectra, as mentioned previously, signals corresponding to PNb were straightforwardly identified (supplementary information Figure S4). Similarly, the *cis/trans* ratio is around 60/40 and stays relatively constant with the irradiation time (Table 2). The molecular weights determined by SEC range between 160 and 20 kg/mol and seem to decrease with time. This phenomenon is explained by the increasing difficulty of solubilizing completely the polymers (particularly those of high molecular weight) in the SEC solvent at high monomer conversion. The real molecular weights are thus probably much higher than

the measured ones. All of these results are in agreement with a better stability of the active species. For the rest of the study irradiance has been fixed at 25 mW/cm^2.

Table 2: Characteristics of the obtained polymers with the catalytic system $IMesH^+BPh_4^-$ /ITX/$[RuCl_2(pCy)]_2$ (5/2.5/1 equiv.) for the polymerization in miniemulsion. Sonication time 10 min, irradiance 25 mW/cm².

Irradiation time (min)	2	5	10	15	20	30	45	60	90
Nb conversion (%)	19	39	58	65	69	74	81	84	91
$M_{n;th}$ (kg/mol)*	19	37	56	62	66	71	78	81	87
$M_{n;expcor}$ (kg/mol)**	108	68	161	81	61	51	26	22	21
Đ	2.77	3.06	2.25	2.42	2.95	2.15	3.11	4.19	2.25
$\%_{cis}$***	62	63	62	63	63	65	66	67	67

* $M_{n;th}=(\pi_{Nb}\times M_{Nb}\times n_{Nb})/(2\times n_{[RuCl2(pCy)]2})$ where π_{Nb} is the Nb conversion, M_{Nb} is the molecular weight of Nb, n_{Nb} is the initial amount of Nb, $n_{[RuCl2(pCy)]2}$ is the initial amount of $[RuCl_2(pCy)]_2$
** Determined by SEC (PS eq.) and corrected: $M_{real}=M_{n;expcor}=M_{measured}/2$
*** $\%_{cis}=I_{cis}/(I_{cis}+I_{trans})$ where I_{cis} is the integration on the ^{1}H NMR spectrum of the signal corresponding to the protons of the *cis* double bonds at 5.21 ppm and I_{trans} is the integration of the signal of the protons of the *trans* double bonds at 5.35 ppm.

3.3- Influence of NHC ligand:

In this part, we have studied the influence of the $IMesH^+BPh_4^-$ /ITX ratio on the polymerization. A trial with a $IMesH^+BPh_4^-$/ITX/$[RuCl_2(pCy)]_2$ molar ratio of 5/5/1 has been performed (Figure 4, red curve) in order to produce more NHC. High conversion (85 %) was achieved after only 15 min of irradiation (versus 65 % after 15 min with a 5/2.5/1 molar ratio).

The ^{1}H NMR spectrum of the polymer samples exhibits signals corresponding to the PNb (supplementary information, Figure S5). Surprisingly, the cis/trans ratio changes with irradiation time. For short irradiation time (< 15 min) the *cis/trans* ratio stays constant at around 70/30 but progressively decreases with time to reach 60/40 after 90 min of irradiation (Table 3). This behavior suggests the participation of inter and intramolecular

chain transfer reactions.[22] Moreover, the analysis of the evolution of the molecular masses measured by SEC confirms this hypothesis (Table 3).[23] Indeed, the experimental mass decreases with the irradiation time whereas the dispersity increases. In addition, the sample obtained for a short irradiation time of 5 min shows a molar mass closer to the theoretical value. To conclude on this part, the modification of the $IMesH^+BPh_4^-$ /ITX ratio makes possible the achievement of an almost complete monomer conversions within 30 min, which has never been performed yet for the miniemulsion ROMP of Nb using such kind of initiator.

Table 3: Characteristics of the obtained polymers with the catalytic system $IMesH^+BPh_4^-$ /ITX/$[RuCl_2(pCy)]_2$ (5/5/1 equiv.) for the polymerization in miniemulsion. Sonication time 10 min, irradiance 25 mW/cm².

Irradiation time (min)	5	10	15	20	30	45	60	90
Nb conversion (%)	23	60	88	90	94	94	93	95
$M_{n;th}$ (kg/mol)*	22	58	84	86	90	90	89	91
$M_{n;expcor}$ (kg/mol)**	34	16	-	7.9	11	13	13	-
Đ	2.47	2.68	-	1.95	2.62	4.51	4.68	-
$\%_{cis}$***	69	68	66	64	62	63	64	62

* $M_{n;th}=(\pi_{Nb}\times M_{Nb}\times n_{Nb})/(2\times n_{[RuCl2(pCy)]2})$ where π_{Nb} is the Nb conversion, M_{Nb} is the molecular weight of Nb, n_{Nb} is the initial amount of Nb, $n_{[RuCl2(pCy)]2}$ is the initial amount of $[RuCl_2(pCy)]_2$
** Determined by SEC (PS eq.) and corrected: $M_{real}=M_{n;expcor}=M_{measured}/2$
*** $\%_{cis}=I_{cis}/(I_{cis}+I_{trans})$ where I_{cis} is the integration on the ^1H NMR spectrum of the signal corresponding to the protons of the *cis* double bonds at 5.21 ppm and I_{trans} is the integration of the signal of the protons of the *trans* double bonds at 5.35 ppm.

3.4- Influence of ruthenium pre-catalyst:

The last parameter studied is the nature of the ruthenium dimer pre-catalyst. Indeed, in the previous work, it has been proved that $[RuCl_2(pCy)]_2$ alone can catalyze the ROMP of Nb in

miniemulsion, leading to a competitive initiation mechanism when employed with the IMesH^{+}BPh$_4^{-}$/ITX system. On the contrary, with [RuI$_2$(*p*Cy)]$_2$ alone, no Nb conversion was observed. Nevertheless, with this pre-catalyst, in presence of IMes^{+}BPh$_4^{-}$/ITX, a Nb conversion of only 30 % was reached.[19] Figure 5 shows Nb conversion as a function of irradiation time using the photocatalytic system IMes^{+}BPh$_4^{-}$/ITX/[RuI$_2$(*p*Cy)]$_2$ (5/5/1 equiv.). Conversions around 40-50 % were achieved after 90 min of irradiation.

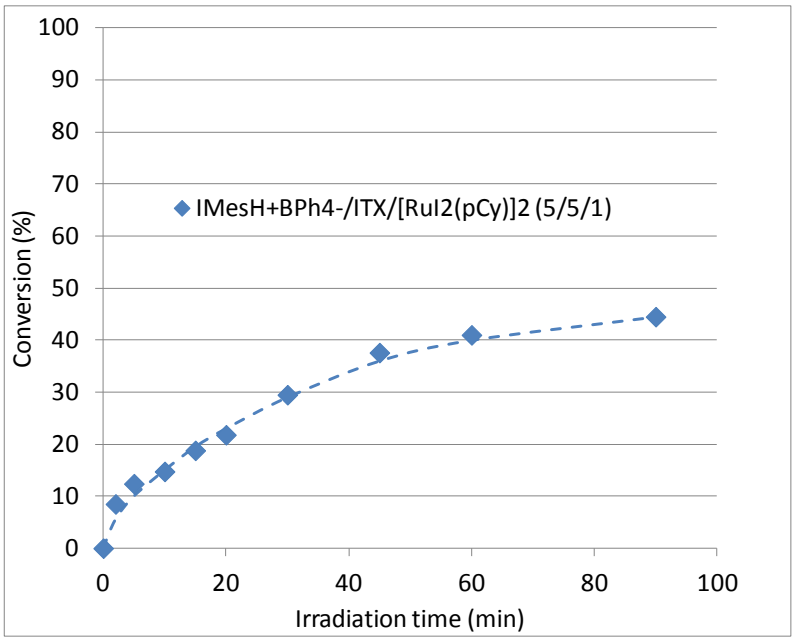


Figure 5: Nb conversion as a function of the irradiation time for the miniemulsion ROMP with the catalytic system IMes^{+}BPh$_4$/ITX/[RuI$_2$(*p*Cy)]$_2$ (5/5/1 equiv.); irradiance 25 mW/cm²; sonication time 10 min.

^{1}H NMR spectrum of the obtained polymers exhibits the corresponding signals of the PNb (supplementary information, Figure S6). However, contrary to the polymer obtained with IMesH^{+}BPh$_4^{-}$/ITX/[RuCl$_2$(*p*Cy)]$_2$ three-components initiator, the polymer exhibits a majority of *trans* unsaturations (from 72 to 52 %) and the *cis/trans* ratio tends to increase with irradiation time (Table 4). Regarding the experimental molecular masses ($M_{n;exp}$), they are

closer to theoretical ones ($M_{n;th}$) than in all previous experiments and tend to decrease with irradiation time after 30 min, which goes in the direction of chain degradations (Table 4).

Table 4: Characteristics of the obtained polymers with the catalytic system $IMesH^+BPh_4^-$ /ITX/$[RuI_2(pCy)]_2$ (5/5/1 equiv.) for the polymerization in miniemulsion. Sonication time 10 min, irradiance 25 mW/cm²

Irradiation time (min)	2	5	10	15	20	30	45	60	90
Nb conversion (%)	8	12	15	19	22	29	37	41	44
$M_{n;th}$ (kg/mol)*	8.1	12	14	18	21	28	36	39	43
$M_{n;exp}$ (kg/mol)**	-	21	23	32	34	47	28	33	31
Đ	-	1.85	2.44	2.28	3.64	4.35	2.44	2.31	2.41
$\%_{cis}$***	28	27	42	41	45	43	41	43	48

* $M_{n;th}=(\pi_{Nb}\times M_{Nb}\times n_{Nb})/(2\times n_{[RuCl2(pCy)]2})$ where π_{Nb} is the Nb conversion, M_{Nb} is the molecular weight of Nb, n_{Nb} is the initial amount of Nb, $n_{[RuI2(pCy)]2}$ is the initial amount of $[RuI_2(pCy)]_2$
** Determined by SEC (PS eq.) and corrected: $M_{real}=M_{measured}/2$
*** $\%_{cis}=I_{cis}/(I_{cis}+I_{trans})$ where I_{cis} is the integration on the ^1H NMR spectrum of the signal corresponding to the protons of the *cis* double bonds at 5.21 ppm and I_{trans} is the integration of the signal of the protons of the *trans* double bonds at 5.35 ppm.

The mechanism of olefin metathesis has been investigated extensively by various teams.[22, 24-27] It has been reported that the nature of the halide ligands can have an effect on the metathesis activity. In particular, it has been shown that exchanging Cl ligands for less electronegative Br or I yielded less reactive active species.[28-30] Additionally, Ru-catalysts containing non-chelated ligand generally favor the formation of trans products[24-26.] Nevertheless, the stereoselectivity of catalyst varies significantly with the ligand, monomer, temperature and solvent. It seems that with our catalytic system $IMesH^+BPh_4^-$ /ITX/$[RuX_2(pCy)]_2$, the generally accepted bottom-bond[24,26,31] pathway (olefin coordination

to the ruthenium-carbene occurs preferentially from one side to generate *trans*-ruthenacyclobutane[32]), is more favorable with iodine than with the less bulky chlorine atom.

It is well known that the *cis*/*trans* ratio has a large influence on the physical properties (melting and glass transition temperature) and on the mechanical properties of the final materials like shock absorption, which is one of the most interesting characteristics of ROMP polymers like PNb.[33] Thus, with these systems, it is easily possible to modulate and control the microstructure of the polymers and consequently the physical and mechanical properties of the final materials just by changing the nature of the ruthenium pre-catalyst, which is essential for an industrial transfer.

4- Conclusion:

In this contribution, the ROMP of a Nb miniemulsion in an annular photo-reactor, initiated with a three components photo-latent system $IMesH^+BPh_4^-$/ITX/$[RuX_2(pCy)]_2$ (X: Cl or I), has been described. On a mechanistic point of view, $IMesH^+BPh_4^-$ irradiated at 365 nm in presence of ITX allows the release of the carbene IMes. The carbene associates with ruthenium dimer pre-catalyst $[RuCl_2(pCy)]_2$ or $[RuI_2(pCy)]_2$ to form the Noels' type catalysts $(IMes)Cl_2Ru(pCy)$ or $(IMes)I_2Ru(pCy)$, well-known to be active for the initiation of Nb ROMP. In a previous study, we described the optimization of the miniemulsion formulation, allowing us to obtain a reasonable efficiency of this kind of system in miniemulsion ROMP and PNb latex with particle of about 100 nm diameter.

Here, the use of an annular reactor allowed scaling-up of the reaction and an improvement of experimental conditions to perform ROMP, allowing the polymerizations to be performed under inert atmosphere and under stirring. These conditions resulted in the improvement of

the Nb conversions, the production of more important batches and an optimization of the irradiation, making this system industrially transferable.

In a first part of this contribution, the ability to obtain polynorbornene latex from irradiation of Nb miniemulsion of 100 nm with an annular reactor was proved. By using the initiating system $IMesH^+BPh_4^-$/ITX/$[RuCl_2(pCy)]_2$, polymers with a majority of cis double bonds were formed. In a second part, different parameters (irradiance, $IMesH^+BPh_4^-$/ITX ratio or nature of the ruthenium pre-catalyst) have been studied and their influence on the Nb conversion profile and the characteristics of the formed polymers have been investigated. Thereby, high Nb conversions could be reached very quickly: more than 90 % after 20 min of irradiation at 25 mW/cm^2. To the best of our knowledge, this level of conversion was very rarely reported in the literature for the ROMP of a Nb miniemulsion. Moreover, correlation could be made between the polymer microstructures and the initiation mechanism.

Finally, by changing the ruthenium pre-catalyst ($[RuCl_2(pCy)]_2$ or $[RuI_2(pCy)]_2$), it has been demonstrated that it is possible to modulate and control the cis/trans ratio of the obtained polymer and thus probably the physical properties of the final materials. Therefore, the good understanding of this new photo-latent system for the initiation of the miniemulsion ROMP of Nb allows the production of PNb latex with high Nb conversion and with tunable and controlled microstructure. It gives access to a new range of polymer latexes having high interest industrially in the field of bioactive coatings or as carrier for biomedical applications.

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Conflicts of interest

There are no conflicts to declare.

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