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Nickel-Catalyzed Supported ATRP of Methyl Methacrylate Using Cross-Linked Polystyrene Triphenylphosphine as Ligand

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ABSTRACT: A new supported catalytic system efficient for synthesizing methacrylate-based (co)polymers is described. This catalyst consists of nickel(II) bromide immobilized onto a polystyrene resin carrying triphenylphosphine moieties (PS-PPh_3/$NiBr_2$). This system was first used for promoting atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) initiated by ethyl 2-bromoisobutyrate (EBr^{i}B) in toluene. Used without any additional reagent, this supported catalyst did not promote controlled ATRP of MMA as attested by the low initiation efficiency and the broad polydispersity indices. However, when triphenylphosphine ligand was added, poly(methyl methacrylate) (PMMA) chains of low polydispersity indices were readily recovered, the molecular weight of which linearly increased with monomer conversion and agreed with the expected values. The as-recovered polymers proved to be almost completely deprived of residual transition-metal catalyst. Moreover, the recovered supported transition-metal complex maintained its catalytic activity for additional polymerization reactions without any further addition of fresh catalyst. Only soluble ligand was added in conjunction to monomer, initiator, and solvent to maintain the control over the molecular parameters in terms of molar masses as well as molecular weight distributions.

Introduction

Since its discovery in 1995 by Matyjaszewski[1] and Sawamoto,[2] the atom transfer radical polymerization (ATRP) has drawn much attention for controlling the (co)polymerization of many different vinyl monomers. Indeed, numerous styrenic, acrylic, and methacrylic monomers have been successfully polymerized by ATRP leading to polymers with controlled molecular weights and very narrow polydispersity indices ($M_w/M_n < 1.3$). Various transition-metal-based catalysts have been developed since that time using ruthenium,[3] nickel,[4] iron,[5] copper,[6] rhodium,[7] and rhenium.[8] However, all these catalysts display rather low catalyst efficiency, and thus a high catalyst concentration is required. The high catalyst residues color the final product, and costly additional steps are needed to remove these transition-metal salts. A potential way to overcome this drawback is to support the catalyst onto a solid carrier, which could be readily removed out from the final product and ideally be recycled for any further polymerization reactions. Some supported catalytic systems have been reported. Most of them are based on copper bromide ligated by immobilized nitrogenated ligands. For instance, the first supported catalytic system was reported by Haddleton et al. in 1999. They developed catalysts based on copper(I) bromide (CuBr) and alkylpyridylmethanimines, i.e., Schiff's base ligands for promoting the supported ATRP (SATRP) of methyl methacrylate (MMA) in toluene.[9] Zhu et al. reported the SATRP of MMA catalyzed by CuBr immobilized onto silica gels surface-grafted with tetraethyldiethylenetriamine and di(2-picolyl)amine via poly(ethylene glycol) spacers.[10] Quite simultaneously, Matyjaszewski et al. reported the controlled polymerization of MMA with CuBr immobilized onto 4,4′-dimethyl-2,2′-bipyridine functionalized Merrifield resins in the presence of a tiny amount of soluble (ligated and oxidized) catalyst ($CuBr_2$/tris(2-(dimethylamino)ethyl)amine).[11] The supported catalytic systems used in SATRP are essentially based on copper complexes. Supported catalytic systems based on other transition metal complexes have not been the object of a lot of attention, at least seldom reported in the open scientific literature, furthermore with very low catalytic efficiency and control. For instance, Haddleton et al.[12] reported the use of ruthenium(II) supported catalyst for the ATRP of MMA. However, the number-average molecular weights of the recovered PMMA chains were higher than predicted ones and the polydispersity indices quite broad ($M_w/M_n > 1.5$). Verpoort et al.[13] studied a ruthenium(II) chloride catalyst immobilized onto a mesoporous zeolite support. Even though this supported catalyst proved to promote the ATRP of styrene, MMA, and acrylonitrile with a good catalytic activity, it did not allow for controlling the polymer molecular parameters as attested by broad polydispersity indices.

This paper investigates another supported catalytic system, i.e., a nickel-based transition-metal catalyst ligated by swollen cross-linked diphenylphosphinopolystyrene beads. With added triphenylphosphine, this catalytic complex proved very high efficiency in controlled SATRP of MMA as recently communicated.[14] This observation prompted us to investigate in more detail the related polymerization process in terms of control over the PMMA molecular weight and molecular weight distribution and the effect of various experimental parameters such as nature and content of purposely added free (soluble) phosphine, reaction time, and recycling experiments. An overall mechanism will be discussed as highlighted by some more targeted polymerization and characterization experiments.

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Experimental Section

Materials. Diphenylphosphinopolystyrene (PS-PPh$_3$) (2.18 mmol of P/g; 1% cross-linked) was purchased from Argonaut Technology. Dibromobis(triphenylphosphine)nickel(II) (NiBr$_2$(PPh$_3$)$_2$) (99%) and ethyl 2-bromoisobutyrate (EBr^{i}B, 98%) were purchased from Sigma-Aldrich. Nickel(II) bromide (NiBr$_2$) (99%), tricyclohexylphosphine (PCh$_3$) (97%), triphenylphosphine (PPh$_3$) (99%), toluene (99.5+%), and methyl methacrylate (MMA, 99%) were purchased from Acros-Organics. The cross-linked polystyrene support (PS-PPh$_3$), EBr^{i}B, PCh$_3$, and the catalysts were used as received without any further purification. Toluene and MMA were passed through a column of basic alumina to remove the stabilizers, bubbled with nitrogen, and stored under slight nitrogen overpressure. PPh$_3$ was recrystallized from ethanol.

Characterization. Nuclear magnetic resonance (NMR) spectra were recorded in CDCl$_3$ using a 300 MHz Bruker spectrometer. Molecular weights and molecular weight distributions were measured by size exclusion chromatography (SEC) in tetrahydrofuran (THF) at 35 °C (flow rate: 1 mL/min) using a Polymer Lab SEC system equipped with a Basic-Marathon autosampler, a guard column (PLgel 10 μm 50 × 7.5 mm), two mixed-B columns (PLgel 10 μm 300 × 7.5 mm, linear columns for separation of molecular weights ranging from 300 to 4×10^6), and a differential refractive index detector (PL-RI). Molecular weights were calibrated using linear PMMA standards in the range 600−1 700 000 g mol^{-1}. ICP measurements were performed on a Jobin Yvon 35+ inductively coupled plasma atomic emission spectrophotometer calibrated with Jobin-Yvon ICP standards in toluene solution. Samples were prepared by dissolving ~50 mg of polymer sample in toluene and then diluting the solution up to 50 mL with toluene. Scanning electron microscopy (SEM) pictures were recorded with a JEOL JSM 6100 under 10 or 5 kV after 230 Å gold coating.

Supported ATRP of Methyl Methacrylate. Typically, 0.64 g of PS-PPh$_3$ (1.4 mmol of PPh$_3$), 0.05 g of NiBr$_2$ (0.23 mmol), and a magnetic stirring bar were introduced in a glass tube reactor equipped with a three-way stopcock. Three nitrogen/vacuum cycles were performed. 5 mL of toluene, 5 mL of MMA (46.75 mmol), 34 μL of EBr^{i}B (0.23 mmol), and 0.73 g of PPh$_3$ (2.8 mmol) were added in a separated flask and bubbled with nitrogen before being transferred in the glass tube reactor by using a previously flame-dried stainless steel cannula. Complexation of the catalyst to the support was considered to be instantaneous as attested for the direct coloration of the polystyrene support. The mixture was subsequently heated to the desired temperature (90 °C) under magnetic stirring. Samples were withdrawn at different time intervals to determine the monomer conversion (by proton nuclear magnetic resonance, ^{1}H NMR, from the relative intensities of the characteristic signal of the methyl groups ($-$C(O)OCH_3) from the PMMA polymer ($\delta \sim 3.6$ ppm) and the residual MMA monomer ($\delta \sim 3.75$ ppm)), number-average molecular weight (M_n), and molecular weight distribution (M_w/M_n) (by SEC). After 6 h, the polymerization reaction was stopped by cooling the glass tube reaction in liquid nitrogen, and after the support settled, the polymer solution was removed out under a slight nitrogen overpressure via a stainless steel cannula. The catalytic support was washed with extra solvent and dried under vacuum while the polymer solution was characterized by ^{1}H NMR, reaching 59% of monomer conversion. After polymer precipitation in heptane, filtration, and drying under reduced pressure, the molar mass of PMMA as denoted in Table 2 was determined by size exclusion chromatography with reference to PMMA standards (M_n = 11 200).

For catalyst recycling experiments, the recovered catalytic support was used without any other treatments (e.g., no further addition of catalyst), just by adding under nitrogen flow the required quantities of solvent, MMA, initiator, and PPh$_3$.

Removal of the Supported Catalytic System from the "Growing" Polymer Solution. After a 30 min polymerization time, the supported catalyst was allowed to settle and the supernatant removed out under nitrogen flow and transferred into a second glass tube nitrogen purged and heated at the desired temperature (90 °C). The remaining solution was allowed to further polymerize under stirring, and aliquots were withdrawn at different time intervals as previously described.

Table 1. Supported Atom Transfer Radical Polymerization (SATRP) of Methyl Methacrylate (MMA) in Toluene Initiated by Ethyl 2-Bromoisobutyrate (EBr^{i}B) and Using Diphenylphosphinopolystyrene Resin (PS-PPh$_3$) as Ligand[a]

entry	catalyst	t (h)	conv[b] (%)	$M_{n,theor}$[c]	$M_{n,exp}$[d]	M_w/M_n[d]
1	NiBr$_2$(PPh$_3$)$_2$	8	60	12200	13600	1.13
2	PS-PPh$_3$/NiBr$_2$(PPh$_3$)$_2$	2	15	3200	4700	bimodal
3		4	29	6000	6000	bimodal
4		6	37	7600	7600	bimodal
5		24	76	15400	14600	1.88

[a] Conditions: 90 °C, [MMA]$_0$ = 4.68 M, [MMA]$_0$/[EBr^{i}B]$_0$/[NiBr$_2$]$_0$/[PS-PPh$_3$]$_0$ = 200/1/1/6. [b] Determined by proton nuclear magnetic resonance (^{1}H NMR) (see Experimental Section). [c] Theoretical number-average molecular weight: $M_{n,theor} \sim [MMA]_0/[EBr^iB]_0 \times \text{conversion} \times MW_{MMA}$. [d] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) as determined by size exclusion chromatography (SEC) using poly(methyl methacrylate) (PMMA) standards.

Table 2. Supported Atom Transfer Radical Polymerization (SATRP) of Methyl Methacrylate (MMA) in Toluene Initiated by Ethyl 2-Bromoisobutyrate (EBr^{i}B) and Catalyzed by Nickel(II) Bromide Ligated by Diphenylphosphinopolystyrene Resin (PS-PPh$_3$/NiBr$_2$) in the Presence of Soluble Triphenylphosphine (PPh$_3$, L′)[a]

entry	[L′]$_0$/[C]$_0$[b]	t (h)	conv[c] (%)	$M_{n,theor}$	$M_{n,exp}$[d]	M_w/M_n[d]
1	2	2	15	3200	4700	bimodal
2		4	29	6000	6000	bimodal
3		6	37	7600	7600	bimodal
4		24	76	15300	14600	1.88
5	6	2	25	5200	5100	1.34
6		4	34	7000	7100	1.29
7		6	46	9400	9300	1.26
8		24	86	17400	17900	1.35
9	12	2	27	5600	6100	1.15
10		4	45	9200	8900	1.14
11		6	59	12000	11200	1.15

[a] Conditions: 90 °C, [MMA]$_0$ = 4.68 M, [MMA]$_0$/[EBr^{i}B]$_0$/[NiBr$_2$]$_0$/[PS-PPh$_3$]$_0$ = 200/1/1/6. [b] C = NiBr$_2$; L = PS-PPh$_3$; L′ = free added PPh$_3$. [c] Determined by proton nuclear magnetic resonance (^{1}H NMR). [d] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) as determined by size exclusion chromatography (SEC) using poly(methyl methacrylate) (PMMA) standards.

Results and Discussion

In the present study, a commercially available diphenylphosphinopolystyrene resin (PS-PPh$_3$), 1% cross-linked beads, was investigated as support for transition-metal-based catalysts. Ruthenium-, iron-, and nickel-based catalysts were first investigated.[15] From these complexes, nickel bromide ligated by triphenylphosphine, NiBr$_2$(PPh$_3$)$_2$, appeared to be the most efficient. Thus, simply in the presence of soluble ligands, this catalyst promotes fast and controlled ATRP of MMA as initiated by ethyl 2-bromoisobutyrate, in agreement with previously published data[16] (see Table 1). Indeed, the initiation efficiency ($f = M_{n,theor}/M_{n,exp}$) is close to unity, attesting for almost quantitative initiation processes while maintaining narrow molecular weight distribution (see entry 1 in Table 1).

Use of Supported Catalytic Systems. NiBr$_2$(PPh$_3$)$_2$ was used in the presence of PS-PPh$_3$ as ligand for

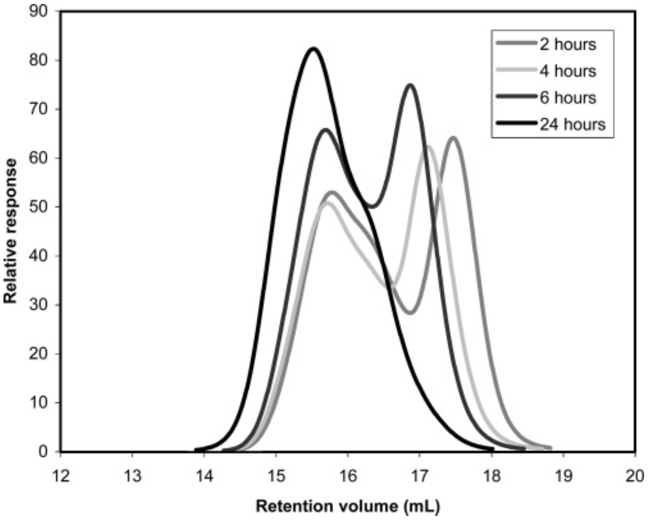


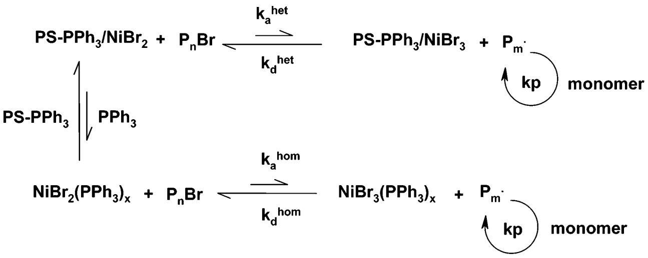
Figure 1. Size exclusion chromatograms of poly(methyl methacrylate) (PMMA) samples obtained by supported atom transfer radical polymerization (SATRP) in toluene, at 90 °C, initiated by 2-ethyl bromoisobutyrate and catalyzed by polystyrene−PPh_3/$NiBr_2(PPh_3)_2$.

promoting the SATRP of MMA as initiated by ethyl 2-bromoisobutyrate (EBr^iB). 6 equiv of immobilized triphenylphosphine was used compared to the catalyst in order to ensure a coordination of the transition-metal salt as complete as possible. The reaction was performed in toluene at 90 °C by withdrawing samples at different time intervals. At the beginning of the reaction, an almost instantaneous dark coloration of the polystyrene resins attested for the strong anchoring of the transition-metal complex onto the swollen support.

Supporting $NiBr_2(PPh_3)_2$ onto PS-PPh_3 did not lead to the expected controlled polymerization of MMA in comparison with the homogeneous catalyst (see entry 1, Table 1). Indeed, the PMMA molecular weight distributions were quite broad and even bimodal in some cases. However, the PMMA samples interestingly displayed molecular weight in the same range than the expected values assuming a quantitative initiation step and a controlled polymerization process, e.g., after 24 h, $M_{n,theor} = 15\,400$ and $M_{n,exp} = 14\,600$ (see entry 5, Table 1); however, the polydipersity index remained quite high ($M_w/M_n = 1.88$). From the SEC chromatograms shown in Figure 1, already at low monomer conversion a broad peak appeared at low elution volume and thus at high molar masses. A narrower signal also shows up at higher elution volume (lower molar masses) and seems to progressively join the first one at higher molecular weight, therefore moving from bimodality to a monomodal molecular weight distribution with an average number molar mass close to the theoretical value.

To account for these observations, one can suspect the presence of some "free" soluble triphenylphosphine (PPh_3) that could be responsible for such a relative control over the polymerization reaction at least in terms of molecular weight. This free PPh_3 could be in situ generated by displacing one or more PPh_3 groups of the added soluble transition-metal complex ($NiBr_2(PPh_3)_2$) along with the nickel bromide coordination onto the swollen support. Accordingly and in order to assess the role of soluble PPh_3, some further investigations have been performed by complexing $NiBr_2$ onto the polystyrene beads in the presence of given amount of purposely added "free" soluble PPh_3 (L′ in Table 2).

Scheme 1. Proposed Mechanism for the SATRP As Catalyzed by PS-PPh_3/$NiBr_2$ in Presence of Purposely Added PPh_3



Influence of Gradual Amounts of Purposely Added Soluble Triphenylphosphine. The presence of purposely added free soluble triphenylphosphine (PPh_3) clearly enhances the control over the molecular parameters in terms of initiation efficiency and polydispersity indices (M_w/M_n). All occurs like if free PPh_3, in relatively large quantities (at least 6 equiv compared to Ni catalyst), can tear off the catalyst from the support and catalyze the polymerization of MMA directly in solution. However, the formation of this solubilized nickel catalyst by ligation with free PPh_3 is more likely reversible since the PMMA chains simply isolated by precipitation from heptane proved to be almost deprived of catalyst residues. Indeed, the so-recovered PMMA chains, thus isolated without any specific catalyst extraction, do not display the green color characterizing the PMMA sample prepared via homogeneous ATRP using $NiBr_2(PPh_3)_2$ as the soluble catalyst while keeping all other conditions unchanged (90 °C, toluene, $[MMA]_0/[EBr^iB]_0/[NiBr_2]_0 = 200/1/1$, precipitation from heptane).[14] This observation attests for very low residual catalyst content. The almost colorless polymer solution could be explained by the equilibrium between less active immobilized catalytic sites and in situ generated soluble catalyst species, equilibrium that is more likely shifted toward the immobilized form. Moreover, because of the monomodality of the molecular weight distribution, one can suppose also that the supported catalyst remains inactive in ATRP and rather behaves as a reservoir that delivers, in a reversible way, the active catalyst in solution. A proposed mechanism is given in Scheme 1, where P_nBr stands for ω-bromo-PMMA chains and $P_m^{\bullet}$ for growing polymethacrylate chains (free radically active) while k_a and k_d represent respectively the activation and deactivation rate constants in heterogeneous (het) or homogeneous (hom) conditions. One can thus assume that the polymerization essentially takes place via the solubilized $NiBr_2(PPh_3)_x$ (where x is probably equal to 2), the activity of which is much higher than the heterogeneous PS-PPh_3/$NiBr_2$ catalyst.

By increasing the concentration in soluble triphenylphosphine, one can presumably increase the amount of catalyst in solution, leading to a better control over the molecular parameters of the obtained polymers. 6−12 equiv of soluble PPh_3 (relative to the Ni content) appears to be a good compromise between high level of control over the PMMA molecular parameters and low residual catalyst content in the recovered polymers. In next steps, some more studies have been carried out in order to check the effect of nature of the "free" soluble ligand and recycling of the supported catalyst.

Influence of the "Free" Ligand: Use of Tricyclohexylphosphine. Actually, it is assumed that in the presence of purposely added "free" PPh_3 ligand part of

Table 3. Effect of Catalyst Recycling in Supported Atom Transfer Radical Polymerization (SATRP) of Methyl Methacrylate (MMA) in Toluene Initiated by Ethyl 2-Bromoisobutyrate (EBr^{i}B) and Catalyzed by Nickel(II) Bromide Ligated by Diphenylphosphinopolystyrene Resin (PS-PPh$_3$/NiBr$_2$)in the Presence of Soluble Triphenylphosphine (PPh$_3$)[a]

entry	catalytic system	t (h)	conv[b] (%)	$M_{n,theor}$	$M_{n,exp}$[c]	M_w/M_n[c]
1	1st use	2	27	5600	6100	1.15
2		4	45	9200	8900	1.14
3		6	59	12000	11200	1.15
4	1st recycling	2	26	5400	7900	1.17
5		4	58	11800	11100	1.19
6		6	64	13000	13900	1.17
7	2nd recycling	2	16	3400	7100	1.58
8		4	43	8800	8500	1.47
9		6	59	12000	10100	1.46

[a] Conditions: 90 °C, $[MMA]_0/[EBr^iB]_0/[NiBr_2]_0/[PS\text{-}PPh_3]_0/[free\ PPh_3]_0 = 200/1/1/6/12$, $[MMA]_0 = 4.68$ M. [b] Determined by proton nuclear magnetic resonance (^{1}H NMR). [c] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) as determined by size exclusion chromatography (SEC) using poly(methyl methacrylate) (PMMA) standards.

the supported NiBr$_2$ can be ligated by the soluble phosphine, reversibly yielding NiBr$_2$(PPh$_3$)$_x$ complexes soluble in the polymerization medium and allowing the MMA polymerization from occurring directly in solution. It is thus assumed that the free-radical generation is essentially promoted in solution, by reaction of the bromide-based initiator (or bromide end group of the propagating chains) with the reversibly produced NiBr$_2$(PPh$_3$)$_x$, the deactivation reaction taking place in solution as well.

As shown in Scheme 1, a way to shift the equilibrium toward the soluble catalyst NiBr$_2$(PPh$_3$)$_x$ is to increase the amount of added triphenylphosphine (as described in the previous section). Another potential way to reach this goal is to change the nature of the "free" ligand, i.e., to use a stronger phosphine ligand such as tricyclohexylphosphine (PCh$_3$).

The SATRP of MMA has been carried out using PCh$_3$ as "free" ligand while maintaining all other conditions unchanged (toluene, 90 °C, $[MMA]_0 = 4.68$ M, $[MMA]_0/[EBr^iB]_0/[NiBr_2]_0/[PS{-}PPh_3]_0 = 200/1/1/6$). Clearly, this polymerization proved to be totally out of control. For instance, for a $[PCh_3]_0/[NiBr_2]_0$ molar ratio of 4, the PMMA chains recovered within a 73% conversion after a 6 h reaction displayed a M_n SEC as high as 50 300 (to be compared to the expected $M_{n,theor} = 14\,800$) with a polydispersity index of 3.27. Furthermore, in SATRP reaction attempts conducted in the presence of free PCh$_3$, the recovered support, washed with toluene at the end of the polymerization reaction, was totally discolored. It means that the added PCh$_3$, thus known to be much stronger than PPh$_3$ as ligand, is able to tear off all Ni species from the swollen support. The supported catalyst is thus unusable for any further polymerization experiments.

Even if the use of PCh$_3$ was not successful as "free" soluble ligand for controlling the SATRP of MMA catalyzed by PS-PPh$_3$/NiBr$_2$, it is worth noting that it could represent an efficient procedure to extract the actual amount of Ni catalyst immobilized onto the support for eventually recycling the support itself after elimination of the metal residues.

Recycling of the Supported Catalytic System. Recycling of the nickel-based supported catalytic system has been investigated. Reuses of the PS-PPh$_3$/NiBr$_2$ supported catalytic system have been performed after filtration and washing of the support with toluene under nitrogen flow in order to avoid any metal oxidation and drying under vacuum. Additional polymerization reactions have thus been carried out in the same experimental conditions by adding required amounts of solvent, monomer, initiator, and PPh$_3$ as for the initial polymerization reaction. Whatever the recycling step, no catalyst was added to the reaction medium; the Ni catalyst only comes from the initial immobilization onto the PS-PPh$_3$ support. In the following Table 3, it is assumed that no loss of catalyst species occurred during support filtration and washing steps and that the recovered polymer samples were globally free of residual catalyst. Such an assumption appears to be acceptable as checked by inductively coupled plasma (ICP) analysis (vide infra).

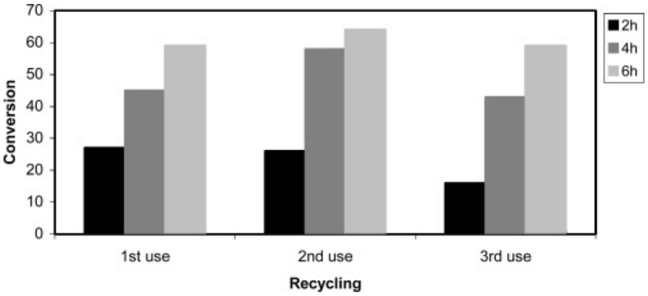


Figure 2. Catalytic activity (recorded at three reaction times) of the PS-PPh$_3$/NiBr$_2$/PPh$_3$ in supported ATRP of methyl methacrylate (MMA).

As shown in Table 3, a very good control in terms of molar masses as well as molecular weight distribution is obtained. The evolution of the number-average molecular weights is maintained close to the theoretical values. Some broadening of the molecular weight distributions is observed starting from the third catalyst use. Such behavior could be explained by a progressive oxidization of the catalyst unavoidable all along the support filtration and washing steps. Moreover, part of the support was systematically lost during each recycling step. Indeed, it is important to remind that each recycling step requires the catalytic support recovering, washing, drying, and swelling for the next polymerization attempt. All of these steps, even though special care was taken, e.g., treatment under nitrogen, were prone to trigger some catalyst deactivation. However, the catalyst maintained a very good activity as attested by the reproducibility of the results in term of monomer conversion. At this stage, such a control has been preserved up to the third use without any noticeable reduction of the catalytic activity (Figure 2). Indeed, after three uses, the catalyst activity remains very good, reaching ca. 60% conversion after 6 h (entry 9 in Table 3). This observation certainly attests for a very limited leaching of the Ni catalyst within the PMMA chains. Indeed, maintaining high catalytic activity means that

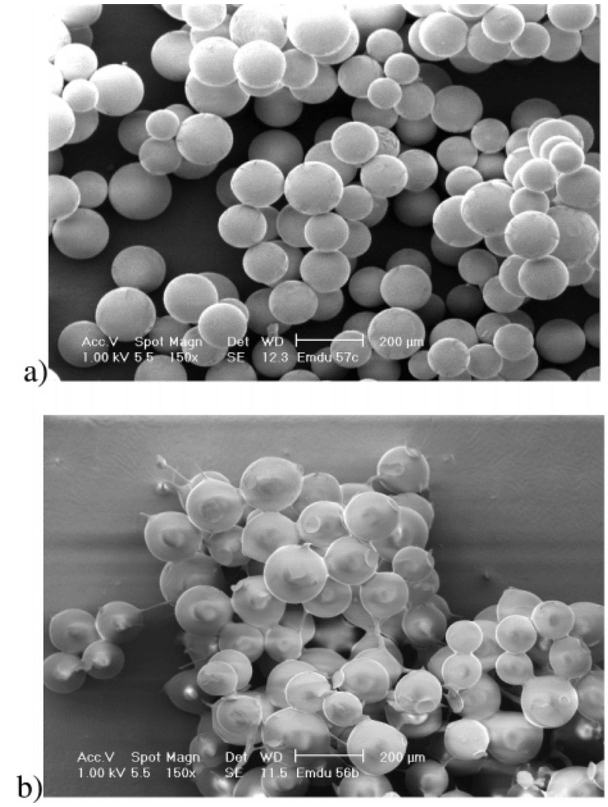


Figure 3. Scanning electron microscopy (SEM) pictures of PS-PPh_3 supports (a) before and (b) after the successive polymerization, filtration, washing, and drying steps.

the major part of the catalyst remains anchored onto the support and is not leached (at least irreversibly) in the polymer solution. This point will be discussed in the next section by ICP measurement of the residual metal content in the polymers.

Supported Catalytic System Morphology. The as-recovered supported catalytic system has been also characterized by scanning electron microscopy (SEM) to check whether the PS-PPh_3 support could be altered by thermal and/or mechanical constraints induced all along the successive polymerization reaction, filtration, washing, and drying steps. SEM observations have been performed after polymerization reactions and are shown in Figure 3.

One can note that the PS-PPh_3 support remains intact. Interestingly, some traces of residual polymer can be observed on some polystyrene beads even after the washing steps.

Inductively Coupled Plasma (ICP) Analysis. To estimate the residual metal content in the polymers synthesized by SATRP and thus simply recovered by precipitation from heptane, some characteristic samples have been analyzed by ICP in toluene using appropriate standard references. Representative results are reported in Table 4.

The amount of residual catalyst is thus very low in PMMA samples as-recovered from the studied SATRP, reaching values as low as 34 ppm. The residual metal content in each PMMA sample represents ca. 1% of the initial amount of catalyst. An homogeneous ATRP of MMA using a similar amount of catalyst at start, i.e., 34 ppm, was carried out for the sake of comparison. The objective of this experiment was to shed some light on the polymerization mechanism of the studied SATRP, i.e., to check whether under such prevailing conditions ($[Ni]_0/[EBr^iB]_{0-0.01}$; $[PPh_3]_0/[Ni]_0 = 6$) one could reach some control over the polymerization. In other words, are we facing a simply conventional homogeneous polymerization process without any role played by the supported catalyst, or does the mechanism pathway schematized in Scheme 1 hold on?

This tiny amount of $NiBr_2$, i.e., 34 ppm, actually strictly corresponds to the quantity leached by the swollen support in SATRP (as measured by ICP). The molecular parameters of the recovered PMMA chains were compared to those obtained via SATRP therefore carried out in the same experimental conditions (i.e., 90 °C, $[MMA]_0 = 4.68$ M, $[MMA]_0/[EBr^iB]_0/[NiBr_2]_0/[PS\text{-}PPh_3]_0 = 200/1/1/6$; see Table 2).

The homogeneous ATRP performed in the presence of such a low content in catalyst ($[Ni]_0/[EBr^iB]_0 \sim 0.01$) does not allow for controlling the polymerization of MMA neither in term of molar masses nor in terms of polydispersity indices (entries 1 and 2 in Table 5). Moreover, one can note that the catalyst activity is much lower compared to the heterogeneous process. No polymer is recovered after 6 h for the homogeneous ATRP (entry 1), and only 16% conversion is reached after 24 h, well lower than the 86% conversion for the heterogeneous process (entry 4). Accordingly, it is clear that the controlled polymerization achieved in the presence of the supported PS-PPh_3/$NiBr_2$ catalyst added with free PPh_3 is certainly not a simple homogeneous ATRP catalyzed by the low content of solubilized $NiBr_2(PPh_3)_x$ catalyst. Indeed, at such a tiny metal content, i.e., with a nickel-to-initiator molar ratio of ca. 0.01, the homogeneous polymerization proved to be very slow and totally out of control. Therefore, one has to take into account an effect of the supported catalytic system in the mechanistic pathway.

Another potential way to confirm this assumption and thus the role of the PS-PPh_3 support in the SATRP process is to separate the "growing" polymer solution from the supported catalytic system at the early stage of the polymerization reaction. Interestingly, a similar experiment was recently reported by Zhu et al.[17] in order to identify the actual active catalytic sites in SATRP of MMA catalyzed by HMTETA/CuBr physically adsorbed to silica gel.[18] The strategy relies upon the hot filtration of the crude (heterogeneous) reaction medium while the polymerization was taking place. The filtrate was collected, and the course of the MMA polymerization was recorded (Table 6). These results have to be compared with those obtained for the same polymerization reaction in which the supported catalytic system was not removed out and thus remained present all along of the polymerization reaction (entries 1−3 in Table 3).

After separation of the supported catalyst, the overall catalyst activity appears slightly reduced, reaching 31% and 48% conversion after 4 and 6 h, respectively (entries 3 and 4 in Table 6), instead of 45% and 59% in the presence of the supported catalyst (entries 2 and 3 in Table 3). Moreover, it is important to note that the control over the molar masses and polydispersity indices is much better when the support remains present in the reaction medium (Figure 4). Indeed, PMMA chains with molecular weight higher than expected values are formed, while the molecular weight distribution increases all along the polymerization, reaching M_w/M_n values higher than 1.5. Instead, quantitative initiation and very narrow molecular weight distribution (M_w/M_n

Table 4. Nickel Content in As-Recovered Representative Poly(methyl methacrylate) (PMMA) Samples As Determined by Inductively Coupled Plasma (ICP) Analysis (see Experimental Section)

entry	reference	$[L']_0/[C]_0$[a]	Ni content (theor) (ppm)[b]	Ni content (ICP) (ppm)	Ni content (ICP) (%)[c]
1	entry 8, Table 2	6	3403	34	1.0
2	entry 3, Table 3	12 (1st use)	4961	46	0.9
3	entry 6, Table 3	12 (2nd use)	4573	57	1.2

[a] L′ = free triphenylphosphine (PPh_3); C = $NiBr_2$. [b] Maximum content of nickel in poly(methyl methacrylate) (PMMA) chains assuming complete metal leaching from the support: $(w_{metal}/w_{monomer})$/conversion. [c] Ni content (ICP)/Ni content (theor).

Table 5. Supported Atom Transfer Radical Polymerization (SATRP) of Methyl Methacrylate (MMA) in Toluene Initiated by Ethyl 2-Bromoisobutyrate (EBr^iB) and Catalyzed by Nickel(II) Bromide Ligated by Triphenylphosphine ($NiBr_2/PPh_3$); Effect of $NiBr_2$ Content at Start

entry	polymerization technique	Ni content (theor) (ppm)[b]	Ni content (ICP) (ppm)	*t* (h)	conv (%)[c]	$M_{n,theor}$	$M_{n,exp}$[d]	M_w/M_n[d]
1	homogeneous ATRP	34[e]		6	0			
2		34[e]		24	16	3400	61500	2.36
3	SATRP	6362		6	46	9400	9300	1.26
4		3403	34	24	86	17400	17900	1.35

[a] Conditions: 90 °C, $[MMA]_0/[EBr^iB]_0 = 200$. [b] Maximum content of nickel in poly(methyl methacrylate) (PMMA) chains assuming complete metal leaching; $(w_{metal}/w_{monomer})$/conversion. [c] Determined by proton nuclear magnetic resonance (^1H NMR). [d] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) as determined by size exclusion chromatography (SEC) using poly(methyl methacrylate) (PMMA) standards. [e] 34 ppm = $[NiBr_2]_0/[EBr^iB]_0 \sim 0.01$, $[PPh_3]_0/[Ni]_0 = 6$.

Table 6. Supported Atom Transfer Radical Polymerization (SATRP) of Methyl Methacrylate (MMA) in Toluene Initiated by Ethyl 2-Bromoisobutyrate (EBr^iB) and Catalyzed by Nickel(II) Bromide Ligated by Diphenylphosphinopolystyrene Resin ($PS-PPh_3/NiBr_2$) in the Presence of Soluble Triphenylphosphine (PPh_3)[a]

entry	*t* (h)	conv[b] (%)	$M_{n,theor}$	$M_{n,exp}$[c]	M_w/M_n[c]	*f*
1	0.5	14	3000	3800	1.27	0.74
removal of the supported catalytic system						
2	2.5	29	6000	8500	1.27	0.68
3	4.5	31	6400	11200	1.39	0.55
4	6.5	48	9800	12800	1.47	0.75
5	24.5	74	15000	19400	1.67	0.76

[a] Conditions: 90 °C, $[MMA]_0/[EBr^iB]_0/[NiBr_2]_0/[PS-PPh_3]_0/[\text{free } PPh_3]_0 = 200/1/1/6/12$, $[MMA]_0 = 4.68$ M. [b] Determined by proton nuclear magnetic resonance (^1H NMR). [c] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) as determined by size exclusion chromatography (SEC) using poly(methyl methacrylate) (PMMA) standards.

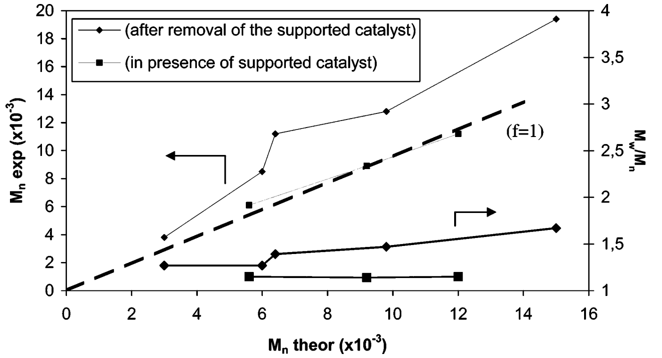


Figure 4. Effect of the presence supported catalyst on number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of PMMA chains in supported atom transfer radical polymerization (SATRP) of methyl methacrylate (MMA) ($f = M_{n,theor}/M_{n,exp}$ = initiation efficiency).

$\sim$ 1.15) are again obtained in the presence of the catalytic support.

In conclusion, a slower and less controlled polymerization takes place after the removal of the catalyst support. But clearly, the overall polymerization rate and the extent of control are both significantly increased when compared to the previously discussed homogeneous ATRP experiment conducted in the presence of a very low content of soluble catalyst ($[Ni]_0/[EBr^iB]_0 \sim 0.01$). In the presence of the $PS-PPh_3/NiBr_2$ supported catalyst added with free PPh_3, all occurs like if the amount of the in situ solubilized catalyst is much higher at the early stage of the polymerization reaction than in the finally recovered polymer. Actually, one cannot exclude that the monomer can influence the metal coordination ability onto the $PS-PPh_3$ support and consequently the catalyst leaching in solution. Consequently, one can suppose that the catalyst concentration in solution could decrease with the monomer concentration and thus decrease during the course of the polymerization reaction. The next section aims at studying such a behavior.

Influence of the "Free" Ligand, Solvent, and Monomer onto the Catalyst Immobilization to the Support. The coordination ability of the catalyst by the phosphine ligands, either soluble (PPh_3) or immobilized onto the $PS-PPh_3$ supports, can be influenced by some parameters such as the nature of the solvent, the presence and quantity of soluble ligand, or the presence of any reagent able to act as coordinating species such as the monomer itself. Indeed, the coloration of the support changes when solvent, monomer, and/or soluble ligand are added to. For instance, $PS-PPh_3$ turns from light yellow to dark orange when $NiBr_2$ is added in toluene. When soluble PPh_3 is added, the support rapidly turns dark green, attesting for the modification of the transition-metal complex (Figure 5).

That is the reason why it seemed interesting to study the influence of toluene, MMA, and PPh_3 on the amount of catalyst that could be leached out during the polymerization reaction. Accordingly, given quantities of support and catalyst ($NiBr_2$) have been mixed with selected amounts of solvent, monomer, and soluble ligand (PPh_3) without any initiator. The experiments were carried out in the presence of inhibitor-deprived MMA (previously passed through basic alumina), but all the reactions were stopped after 2 h in order to limit the extent of thermally promoted free-radical polymerization of MMA. In all these cases, after the support washing step, the filtrates were collected and directly diluted with toluene and analyzed by ICP without any intermediate drying steps (Table 7).

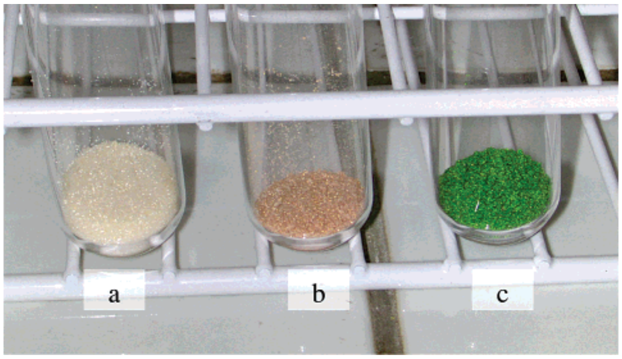


Figure 5. Pictures of (a) PS-PPh_3, (b) PS-PPh_3/$NiBr_2$, and (c) PS-PPh_3/$NiBr_2$/free PPh_3 supports after filtration and drying steps.

Table 7. Influence of Toluene, Methyl Methacrylate (MMA), and Soluble Triphenylphosphine (PPh_3) on the Coordination Ability of $NiBr_2$ onto the Swollen Diphenylphosphinopolystyrene (PS-PPh_3) Support (Suspension of 128 mg of PS-PPh_3 in 2 mL Solution)[a]

entry	toluene (mL)	MMA (mL)	color of the support	PPh_3 (mol equiv/catalyst)	% leached metal[a]
1		2	orange	0	0.19
2		2	green	6	1.25
3		2	green	12	2.89
4	1	1	kaki	0	0.30
5	1	1	green	6	0.52
6	1	1	green	12	0.89
7	2		light green	0	0.05
8	2		green	6	0.11

[a] Conditions: 90 °C for 2 h, $[\text{PS-PPh}_3]_0/[\text{NiBr}_2]_0 = 6$. [b] Weight percentage of the initial $NiBr_2$ content as measured by inductively coupled plasma (ICP) in toluene.

The presence of soluble PPh_3 as well as the presence of MMA both influence the coordination extent of the catalyst onto the support as attested by the color of the supported catalysts. As expected, it comes out that the amount of leached catalyst increases with PPh_3 (entries 7 and 8; 0.11% of leached metal against 0.05% without added PPh_3), but the addition of MMA substantially enhances this effect (entries 5 and 2): 0.52% and 1.25% of leached metal respectively in the presence of 1 and 2 mL of MMA. Consequently, it is not surprising that the polymerization reaction is influenced not only by the purposely added soluble ligand (PPh_3) but also by the nature and the concentration of the monomer. Accordingly and confirming previous observation, the relative content in soluble $NiBr_2(PPh_3)_x$ thus in situ generated owing to the presence of "free" PPh_3 will depend on the starting MMA concentration but will also vary all along the polymerization stage and the concomitant monomer consumption. Such an effect gives credit to the initially proposed mechanism (Scheme 1) and the interrelated equilibria: the monomer concentration affects the content in soluble active catalyst (i.e., produced by leaching from the supported catalyst), which in turn triggers the controlled polymerization of MMA. It results a continuous decrease of the monomer concentration so as at the end of the SATRP, and as a result of these equilibria, the concentration in soluble catalyst is reduced, yielding PMMA chains much less contaminated by metal catalyst residues (ca. 34 ppm, thus about 1% of the starting metal content under the investigated experimental conditions).

Conclusion

A novel diphenylphosphinopolystyrene resin (PS-PPh_3) has been investigated as support for transition-metal complexes able to catalyze the SATRP of methyl methacrylate (MMA). From the literature, it comes out that almost all the reported supported catalytic systems used in SATRP are based on copper bromide ligated by nitrogenated ligands. The PS-PPh_3 allows for coordinating a large range of transition-metal complexes including nickel(II) bromide. Actually, when ligated with PPh_3 nickel(II) bromide, i.e., $NiBr_2(PPh_3)_2$, proved high efficiency for controlling the ATRP of MMA under homogeneous conditions, yielding polymers with very narrow molecular weight distribution with polydispersity indices as low as 1.1. Therefore, it has been decided to coordinate nickel(II) bromide onto swollen PS-PPh_3 beads and to use them as supported catalytic system to promote SATRP of MMA in toluene. Even if the coordination of the metal occurred almost instantaneously as attested by the fast and dark coloration of the polystyrene resin, the SATRP of MMA was not well controlled. Indeed, the so-obtained PMMA showed rather broad molecular weight distributions, however, with average number molar masses close to the theoretical values at least at higher monomer conversion. It was assumed that the presence of "free" soluble triphenylphosphine (PPh_3), in situ generated by displacing one or more PPh_3 groups of the added soluble transition-metal complex ($NiBr_2(PPh_3)_2$) during the coordination of the catalyst onto the support, could enhance the control over the PMMA molecular parameters (M_n, M_w/M_n). Consequently, further investigations have been performed by using the PS-PPh_3/$NiBr_2$ catalytic complex in the presence of gradual amounts of purposely added "free" soluble PPh_3. Interestingly enough, addition of soluble PPh_3 ligands allows for enhancing the control over the SATRP as well as the polymerization kinetics. Indeed, when conducted in the presence of larger amounts of soluble PPh_3 (6−12 equiv, as compared to Ni), the SATRP yielded PMMA chains with very narrow molecular weight distribution and molar masses in perfect agreement with the theoretical ones assuming a controlled process. All occurs like if "free" PPh_3 can tear off the nickel catalyst from the support and catalyze the polymerization of MMA directly in solution. However, the formation of this solubilized nickel catalyst by ligation with PPh_3 is more likely reversible since the PMMA chains simply isolated by precipitation from heptane proved to be poorly contaminated by residual catalyst. Indeed, the PMMA chains thus isolated without any specific catalyst extraction did not show the green color characterizing the PMMA sample prepared via homogeneous ATRP using $NiBr_2(PPh_3)_2$ as the soluble catalyst while keeping all other conditions unchanged. This observation attests for very low residual catalyst content as confirmed by ICP: ca. 1% of the starting catalyst content. It is worth noting that all attempts to carry out the homogeneous ATRP of MMA starting with such a tiny amount of soluble $NiBr_2$/PPh_3 (all other conditions unchanged) failed (i.e., very poor catalyst activity and no control over the molecular parameters). This observation excludes the occurrence of a conventional homogeneous ATRP. As a result, the support should retain its catalytic activity and expectedly should be reusable for any further SATRP. Actually, the recycling of the as-recovered supported catalytic system has been investigated. Very interestingly, when reused in the presence of soluble PPh_3, this supported catalyst proved again high efficiency in terms of activity and control over the PMMA molecular parameters (narrow molecular weight distribution and almost quantitative initiation efficiency). At this stage, such a control has been preserved up to the third use without any noticeable reduction of the catalytic activity. It means that oxidation of the metal complex does not occur, at least at an extent high enough for deactivating (or preventing) the polymerization reaction. Finally, it has been evidenced that, after separation of the supported catalyst, the remaining reaction medium still displayed some catalyst activity. However, this activity is significantly reduced, and the control over the molar masses and polydispersity indices of the PMMA chains is largely affected with molecular weight higher than expected values and broader molecular weight distributions. All occurs like if the amount catalyst in solution was higher at the early stage of the polymerization reaction than the quantity determined in the finally recovered polymer. This could be explained by the presence of the high monomer concentration able to increase the catalyst leaching in solution. Such a behavior was evidenced by measuring the amount of leached catalyst from the support while adding a gradual amount of PPh_3 and/or MMA on PS-PPh_3/$NiBr_2$ in toluene.

This paper has evidenced the high efficiency of PS-PPh_3/$NiBr_2$ as supported catalytic system for promoting controlled SATRP of MMA in toluene in the presence of a given amount of purposely added triphenylphosphine. This catalyst has proved to be readily recycled while maintaining high activity and good control over the molecular parameters. Such a control has been recently extrapolated for synthesizing diblock copolymers such as P[DMS-*b*-MMA] copolymers.[15] The results will be published in a forthcoming paper.

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