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Supported nickel bromide catalyst for Atom Transfer Radical Polymerization (ATRP) of methyl methacrylate

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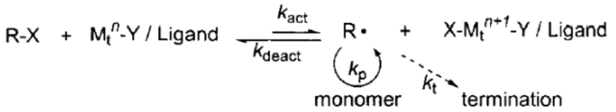
Received (in Cambridge, UK) 22nd December 2003, Accepted 20th January 2004
First published as an Advance Article on the web 13th February 2004

A new supported catalytic system, *i.e.* nickel bromide catalyst ligated by triphenylphosphine (TPP) ligands immobilized onto crosslinked polystyrene resins (PS-TPP) is reported. *Per se*, this catalyst does not allow any control over the polymerization of methyl methacrylate (MMA) initiated by ethyl 2-bromoisobutyrate but, in the presence of a given amount of purposely added free TPP, it promotes controlled ATRP of MMA. Indeed colorless PMMA chains of low polydispersity indices are readily recovered, the molecular weight of which linearly increases with monomer conversion and agrees with the expected values. Recycling of the supported catalyst is evidenced and does not prevent the polymerization from being controlled.

Since its discovery in 1995 by Matyjaszewski[1] and Sawamoto,[2] ATRP has been of great interest to control the polymerization of vinyl monomers. Indeed, various styrenic, and (meth)acrylic monomers have been successfully polymerized by ATRP leading to polymers with controlled molecular weight and narrow polydispersity indices (MWD < 1.3). In the ATRP process, a dynamic equilibrium is established between an active radical ($R^{\cdot}$) and a dormant species (halogenoalkane, R–X) in the presence of a transition metal complex (M_t^n–Y/Ligand) acting as a reversible halogen atom transfer reagent. As a result, the steady-state concentration in radicals is maintained very low and the contribution of irreversible termination reaction is negligible (Scheme 1).

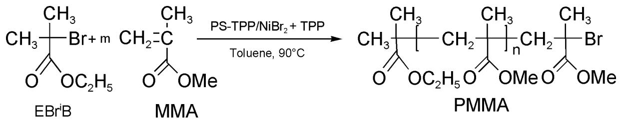
Different transition metal catalysts have been investigated so far which essentially rely upon ruthenium,[3] nickel,[4] iron,[5] copper,[6] rhodium[7] and rhenium.[8] However, all the reported transition metal catalysts have been shown to display rather low catalyst efficiency and thus a high catalyst concentration is required *i.e.*, most often at equimolar levels in regard to R–X initiation species. The high catalyst residues provide final products with a deep color and costly additional steps are necessary in order to remove these transition metal salts. A potential way to overcome this drawback is to support the catalyst on a solid carrier, which could be easily removed from the final product, *e.g.* by filtration, and ideally be recycled for any further polymerization reactions. A few supported catalytic systems have been reported so far,[9–11] all of them being exclusively based on copper bromide ligated by immobilized nitrogenated ligands. However, even if this technique seems to be very attractive, control over the polymerization is often limited by the low mobility of the immobilized catalyst sites. Consequently, the reversible deactivation of the active propagating radical into a dormant species is slowed down, leading to a higher transfer and termination reactions with the consequent lost of polymerization control. Nevertheless, new strategies have been approached in order to improve the control over the supported ATRP of vinyl monomers. Interestingly, Matyjaszewski *et al.* have recently developed a hybrid system composed of an immobilized catalyst, *i.e.* Cu(I) and a given amount of a soluble catalyst precisely in the oxidized state. This soluble ligated Cu(II) catalyst is actually required to accelerate the deactivation process of the growing radical.[11] In an alternative approach, we have investigated a new supported catalytic system built up on nickel bromide and which does not required the addition of soluble nickel-based complexes to give controlled ATRP.



Scheme 1 Atom Transfer Radical Polymerization (ATRP).

This communication aims at reporting on a crosslinked diphosphinopolystyrene supported nickel bromide catalyst able to control the ATRP of MMA in the presence of purposely added "free" soluble triphenylphosphine (TPP) ligand. All the polymerization experiments† were performed at 90 °C in toluene using ethyl 2-bromoisobutyrate as initiator (Scheme 2). Clearly, the addition of "free" soluble TPP in the polymerization medium allows improvement to both catalytic activity and control over the molecular parameters of the synthesized PMMA in term of molar masses (M_n) and polydispersity indices. Table 1 gives evidence for such a positive effect of purposely added TPP and its relative content on the supported ATRP (SATRP) of MMA. Even if the nickel-based supported catalyst when used alone (*i.e.* in the absence of any added TPP) displays rather high catalytic activity reaching 83% of monomer conversion after 24 h, no control can be observed as evidenced by bimodal molecular weight distributions and variable M_n values (entries 1a–c in Table 1).

Interestingly, the addition of soluble TPP ligands allows for enhancing the control over the SATRP as well as the polymerization kinetics. Indeed, after a 4 hour reaction time, the monomer conversion increases from 23% to 45% while the triphenylphosphine concentration is increased from 0 to 12 equivalents in comparison with the initial catalyst concentration. On an other



Scheme 2 Supported ATRP of MMA using ethyl 2-bromoisobutyrate (EBriB) as initiator.

Table 1 SATRP of MMA in toluene, at 90 °C, initiated by ethyl 2-bromoisobutyrate and catalyzed by PS-TPP/NiBr$_2$ in the presence of soluble TPP

Entry	[M]/[I]/[C]/[L]/[L′][a]	*t*/h	Conv.[b] (%)	M_n theor.	M_n exp.[c]	MWD[c]
1a	200/1/1/6/0	2	22	4400	65700	Bimodal
1b	200/1/1/6/0	4	23	4600	184700	Bimodal
1c	200/1/1/6/0	24	83	16600	19600	Bimodal
2a	200/1/1/6/2	2	15	3000	4700	Bimodal
2b	200/1/1/6/2	4	29	5800	6000	Bimodal
2c	200/1/1/6/2	6	37	7400	7600	Bimodal
2d	200/1/1/6/2	24	76	15100	14600	1.88
3a	200/1/1/6/6	2	35	7000	6140	1.31
3b	200/1/1/6/6	4	37	7400	8480	1.24
3c	200/1/1/6/6	6	61	12200	11100	1.22
3d	200/1/1/6/6	24	97	19400	17800	1.43
4a	200/1/1/6/12	2	27	5400	6090	1.15
4b	200/1/1/6/12	4	45	9000	8860	1.14
4c	200/1/1/6/12	6	59	11800	11200	1.15

[a] M; monomer. I; initiator. C; catalyst. L; ligand immobilized onto the support. L′; free TPP. [b] Determined by ^{1}H-NMR. [c] Determined by SEC using PMMA standards.

DOI: 10.1039/b316645g

hand, for SATRP conducted in the presence of larger amounts of soluble TPP, the as-recovered PMMA, characterized by SEC, has monomodal molecular weight distribution and molar masses close to the theoretical ones (entries 3a–d 4a–c). The reaction occurs as if "free" TPP 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 TPP is more likely reversible since the PMMA chains simply isolated by precipitation from heptane proved to be much less contaminated by residual catalyst. Indeed as shown in Fig. 1, the so-recovered PMMA chains (Fig. 1b), thus isolated without any specific catalyst extraction, do not show the green color characterizing the PMMA sample (Fig. 1c) prepared *via* homogeneous ATRP using $NiBr_2(TPP)_2$ as the soluble catalyst while keeping all other conditions unchanged (90 °C, toluene, [M]/[I]/[C] = 200/1/1, precipitation from heptane). This observation attests for a very low residual catalyst as confirmed by ICP (34 ppm in recovered PMMA, thus *ca.* 1 wt% of catalyst at start). For sake of comparison, a PMMA sample obtained by conventional radical polymerization (without any catalyst) has been added as well (Fig 1a). It is worth noting that all attempts to carry out the homogeneous ATRP of MMA starting with such a tiny amount of soluble $NiBr_2$ (all other conditions unchanged) failed, *i.e.*, very poor activity, no control over 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 TPP, this supported catalyst proved again to be of high efficiency in terms of activity and control over the PMMA molecular parameters (narrow molecular weight distribution and *f* values close to unity). At this stage, such 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 to an extent high enough for deactivating (or inhibiting) the polymerization reaction. Moreover, block copolymers have been successfully synthesized by SATRP using the macroinitiator technique. Control over the molar masses as well as the polydispersity indices was as good as for the synthesis of homo PMMA. All these points will be discussed soon.

In conclusion, the presence of free soluble triphenylphosphine (TPP) has advantageously enhanced the control over the molecular parameters in terms of initiation efficiency ($f \approx 1$) and polydispersity indices ($M_w/M_n \approx 1.15$) most likely by reversibly tearing off part of the catalyst from the support. In fact, an equilibrium between homogeneous "free" catalyst and less active immobilized catalyst might occur and could be strongly shifted towards the immobilized form, leading to controlled polymerization of MMA in solution. Moreover, adding "free" TPP in the reaction medium increases the overall polymerization kinetics. Experiments aiming at understanding the actual mechanism of this controlled ATRP are under investigation and will be discussed in a forthcoming paper.

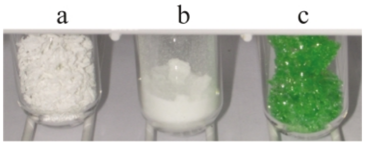


Fig. 1 PMMA samples obtained by a) conventional free-radical polymerization initiated by AIBN, b) SATRP with PS-TPP/$NiBr_2$/TPP, and c) homogeneous ATRP with soluble $NiBr_2(TPP)_2$.

E.D. is much indebted to Dow Corning and "DGTRE-Région Wallonne" for financial support in the frame of his PhD thesis (FIRST Doctorate). Authors are very grateful to "Région Wallonne" and European Community (FEDER, FSE) for general support in the frame of "Objectif 1-Hainaut: Materia Nova". This work was partly supported by the Belgian Federal Government Office of Science Policy (SSTC-PAI 5/3).

Notes and references

† The solid materials (the diphosphinopolystyrene support crosslinked by 1% divinylbenzene and containing 1.51 mmol g^{-1} (batch 1, entries 2a–d) and 2.18 mmol g^{-1} (batch 2, entries 1a–c, 3a–d and 4a–c) of phosphorus atom, catalyst and free ligand when needed) were introduced in a flask before nitrogen/vacuum cycles directly followed by the addition of solvent, monomer and initiator. Sample withdrawals were performed at time intervals to determine conversion (conv.) (by proton nuclear magnetic resonance, ^{1}H-NMR), number average molecular weight (M_n) and molecular weight distribution (MWD) (by size exclusion chromatography, SEC).

‡ Recycling of the supported catalytic systems was performed under N_2: the solution medium was removed by cannula after allowing the support to settle. The support, still carrying the transition metal catalyst, was washed several times with degassed toluene. The support was subsequently dried under vacuum. During all this procedure, the support was kept under nitrogen in order to avoid any deactivation by contact with air. The washed support was then reused for a further polymerization conducted under the same experimental conditions.

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