

New supported-catalytic systems for atom transfer radical polymerization



Claire Bernhardt^{a, b}, Chirine Ben Osman^{a, b}, Bernadette Charleux^c,
François Stoffelbach^{a, b, *}

^a Institut Parisien de Chimie Moléculaire, Sorbonne Universités, UPMC Univ Paris 06, UMR 8232, F-75252 Paris Cedex 05, France

^b Institut Parisien de Chimie Moléculaire, CNRS, UMR 8232, F-75252 Paris Cedex 05, France

^c Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, C2P2, Team LCPP Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France

ARTICLE INFO

Article history:

Received 13 July 2015

Received in revised form

12 September 2015

Accepted 15 September 2015

Available online 18 September 2015

Keywords:

ATRP

Macroligand

Picolyl amine

Silica nanoparticle

Supported catalyst

ABSTRACT

The atom transfer radical polymerization (ATRP) was studied using new well-defined functional copolymers (poly(styrene-co-vinylbenzyl chloride) - Poly(S-co-VBC)- modified by di(2-picolyl)amine) as macroligands. Poly(S-co-VBC) copolymers with various proportions of VBC monomer were prepared either by free radical polymerization or by nitroxide-mediated polymerization using a commercially available alkoxyamine (BlocBuilder®). Macroligands were further obtained by post-modification of poly(S-co-VBC) by di(2-picolyl)amine (DIPA) and were then successfully used for the homogeneous ATRP of methyl methacrylate and styrene. We also investigated the ATRP in heterogeneous conditions with the macroligand being supported onto silica Stöber nanoparticles.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Atom transfer radical polymerization (ATRP) represents one of the most versatile synthetic tools for the preparation of polymer materials with well-controlled molar masses and well-defined structures [1,2]. However, one remaining challenge of this polymerization technique is to separate efficiently the homogeneous catalysts involved from their reaction products. Many purification methods [3] such as postpurification [4,5] and liquid–liquid biphasic separation [6–10] have been developed for the removal of catalysts from polymers but they are too costly to give rise to industrial applications. Another approach is to support the catalyst onto micron-sized particles by immobilization via chemical bonding, allowing the separation of the latter by decantation or centrifugation at the end of the polymerization. Catalysts tethered on solid surfaces such as silica gel, polystyrene beads and Janda Jel resins have been explored for catalyst removal and reuse in ATRP [11]. However, polymers produced from supported catalyst

generally display less controlled molar masses and dispersities than those produced using homogeneous catalysts. This is often attributed to the low mobility of supported catalyst and to a slow deactivation of the growing radical [12]. One approach to improve the control of the polymerization is the addition of soluble deactivator or free soluble ligand in the reaction medium [12–14]. Furthermore, some others catalyst systems combining the advantages of both heterogeneous and homogeneous catalysis, have been developed to try to solve this problem. For examples, thermoresponsive ligands [15,16] or (co)polymers (polyethylene [17] or polyethylene-*b*-poly(ethylene glycol) [18,19]) end-capped with an appropriate ligand were used for the ATRP of methyl methacrylate (MMA). However, their rather tedious preparation or the specific experimental conditions in which they can be used limit their applications. Hitherto, very few studies [20–22] on the use of catalysts immobilized along soluble polymer arms grafted onto a support have been reported (Fig. 1). These hybrid systems seem very promising since they should *a priori* act similarly to homogeneous catalysts leading to more accessibility of the catalyst due to less steric effect of the support which is observed with heterogeneous systems. Buchmeister et al. [20] have developed a system based on poly(4'-(norborn-2-ene-5-ylmethyleneoxy)terpyridine) prepared via ring-opening metathesis polymerization and grafted

* Corresponding author. Institut Parisien de Chimie Moléculaire, Sorbonne Universités, UPMC Univ Paris 06, UMR 8232, F-75252 Paris Cedex 05, France.

E-mail address: francois.stoffelbach@upmc.fr (F. Stoffelbach).

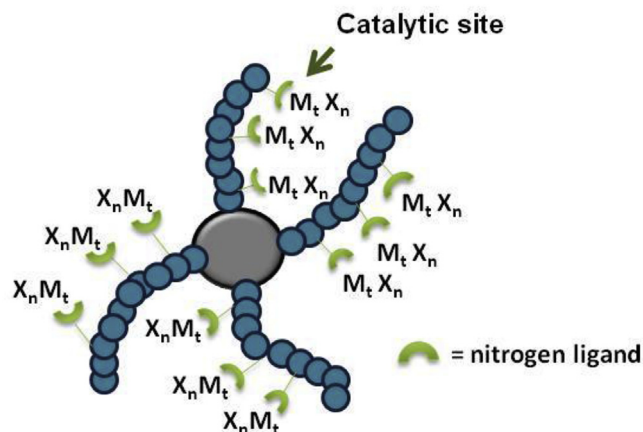


Fig. 1. Catalysts immobilized along soluble polymer arms grafted onto a support.

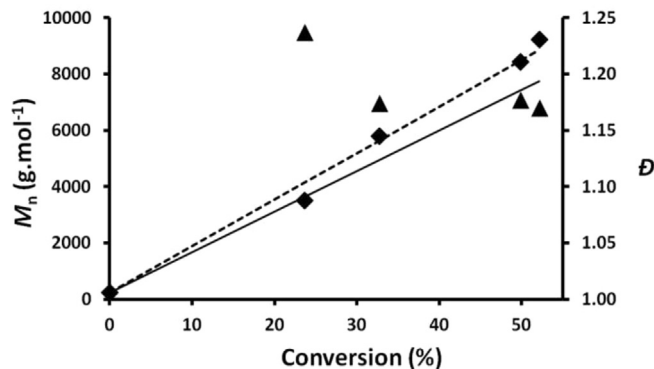


Fig. 4. Evolution of the number-average molar mass, M_n (♦) and dispersity, D (▲) versus monomer conversion for the ATRP (P7) of MMA at 60 °C initiated with MBP. The dashed line corresponds to the theoretical expected M_n vs. conversion with an initiator efficiency factor of 0.87.

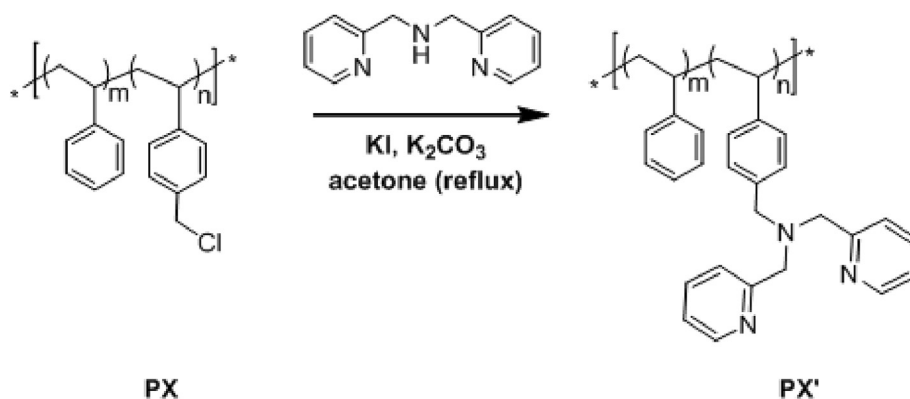


Fig. 2. Synthesis of macroligand by post-modification of poly(*S-co-VBC*) by DIPA.

onto silica particles (40–63 μm). The ATRP of styrene involving the latter catalyst has been achieved, affording poor yield (<35%) and quite high dispersities. This lack of control was attributed to deactivation problems. Fournier et al. [21] have elaborated a supported catalytic system based on (*N,N,N',N'*-tetraethyldiethylenetriamine) ATRP ligand immobilized onto Wang-*g*-poly(2-vinyl-4,4-dimethyl-5-oxazolone) and Wang-*g*-poly(2-vinyl-4,4-dimethyl-5-oxazolone-*stat*-styrene) resins in order to create supported complexing sites for copper bromide. The ATRP of MMA was studied

with these supported ligands but high dispersities were also observed ($D > 2$) and the number-average molar masses were higher than the theoretical ones, indicating an uncontrolled polymerization process. More recently, Detrembleur et al. [22] have successfully used a system composed of CuBr ligated by two different supported fluorinated macroligands (0.06 macroligand nm^{-2} with $M_n = 5$ or 15 kg mol^{-1}) immobilized by “grafting onto” approach onto silica beads (Carbosil, $\sim 0.3 \mu\text{m}$) for the ATRP of 2,2,2-trifluoroethyl methacrylate in super-critical

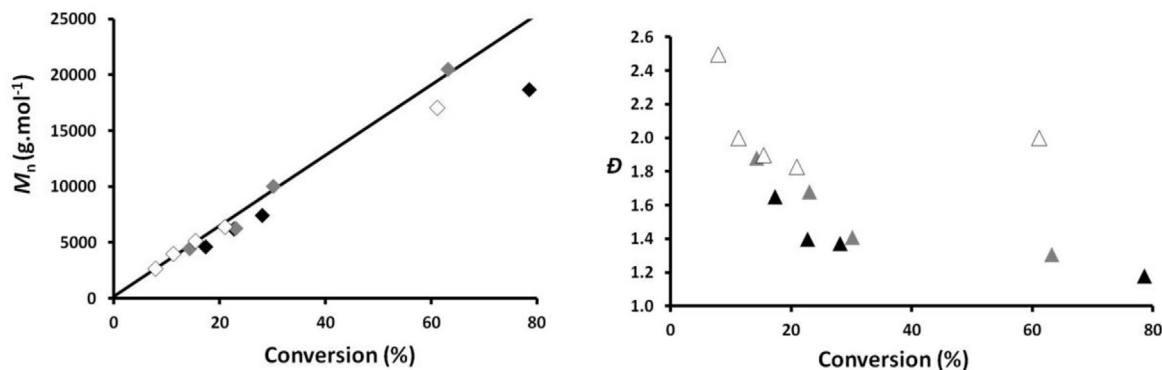


Fig. 3. (Left) Evolution of the number-average molar mass: M_n (P4: ♦, P5: ◊, P6: ○). (Right) dispersity: D (P4: ▲, P5: △, P6: △) versus monomer conversion for the ATRP polymerizations of styrene at 90 °C initiated with BEB.

Download English Version:

<https://daneshyari.com/en/article/5179897>

Download Persian Version:

<https://daneshyari.com/article/5179897>

[Daneshyari.com](https://daneshyari.com)