European Polymer Journal 46 (2010) 2333–2340

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Synthesis of basic molecular brushes: ATRP of 4-vinylpyridine in organic media

Joanna Pietrasik [a,*], Nicolay V. Tsarevsky [b,1]

[a] *Technical University of Lodz, Institute of Polymer and Dye Technology, Stefanowskiego 12/16, 90 924 Lodz, Poland*
[b] *Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA*

ARTICLE INFO

Article history:
Received 8 June 2010
Received in revised form 23 August 2010
Accepted 30 September 2010
Available online 8 October 2010

Keywords:
Molecular brushes
ATRP
4-Vinylpyridine
Stimuli responsive polymers

ABSTRACT

A poly(2-(2-bromopropionyloxy)ethyl methacrylate) (PBPEM) was used as macroinitiator in the synthesis of molecular brushes with poly(4-vinylpyridine) side chains, (P(BPEM-g-4VP). Atom transfer radical polymerization (ATRP) was employed as the polymerization technique. The polymerizations were carried out in DMF at 30 °C using a copper–chloride-based ATRP catalyst, which converted all the dormant polymer chain ends to alkyl chloride groups, thus minimizing branching and crosslinking, which occurred when a copper bromide-based catalyst was employed. Tris(2-pyridylmethyl)amine was selected as the ligand due to the high activity of its Cu^I complex in ATRP as well as its strong binding to both Cu^I and Cu^{II}, which prevented competitive complexation of the monomer or polymer to the metal center. In order to prevent crosslinking via radical coupling, the monomer conversion was kept low (under 3%) and the alkyl chloride end groups of P4VP side chains were converted to alkoxyamines upon activation followed by a reaction with TEMPO radical. Dynamic light scattering measurements showed the hydrodynamic diameter (D_H) of the brushes was pH-dependent. Aggregation of single P(BPEM-g-4VP) brushes in water was very pronounced at high pH values but was observed even when the amount of added HCl was enough to completely protonate the pyridine units ($D_H = 278$ nm).

1. Introduction

The development of controlled/living radical polymerization (CRP) techniques [1–4] has made accessible to synthetic polymer chemists an enormous “tool box”, allowing the synthesis of a variety of well-defined polymers. New materials can be created by precisely controlling parameters such as molecular weight and molecular weight distribution, microstructure, topology and functionality. Among many polymer architecture, such as linear, star, comb, branched, dendritic, or network polymers, densely grafted molecular brushes are very interesting class of materials [5–7]. Their compact structure, very high local concentration of functional groups, and uniformity all lead to special properties that could be potentially used in a wide range of applications, such as unimolecular carriers [8–9], templates [10–12], super-soft materials [13–14] or sensors [15]. Apart from CRP, other techniques such as anionic polymerization, ring-opening metathesis polymerization, or coupling reactions as click chemistry were also successfully used for the synthesis of graft or brush copolymers [16–24].

Three approaches have been used for the synthesis of molecular brushes: grafting from [25–31], grafting onto [22,32–35] and grafting through [36–42] techniques. The synthetic challenges and constraints have been very well described in several reviews [5–6,43]. In brief, in order to obtain uniform molecular brushes, CRP methods have been the synthetic procedures of choice [44]. Atom transfer radical polymerization (ATRP) is one of those techniques

---

[*] Corresponding author. Tel.: +1 48 42 631 3208; fax: +1 48 42 636 2543.

E-mail address: joanna.pietrasik@p.lodz.pl (J. Pietrasik).

[1] Present address: Department of Chemistry, Southern Methodist University, 3215 Daniel Avenue, Dallas, TX 75275, USA.

0014-3057/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2010.09.043

[45–48]. It was already successfully applied for styrene [49], (meth)acrylates [13,50–52], acrylamides [51] as monomers in the synthesis of molecular brushes.

The area of stimuli responsive materials has been developing rapidly and has recently attracted much attention. [53] Temperature [29,54–59], light [60], solvent composition, pH [61–62], ionic strength and magnetic field [63–64] are examples of stimuli that can change properties of responsive materials. Various functional monomers such as 2-(*N*,*N*-dimethylamiono)ethyl methacrylate [51], poly(oligo(ethylene oxide) methyl ether methacrylate) [65–66], isopropylacrylamide [67] were used as building blocks for responsive molecular brushes. Nevertheless, there are some monomers that have not yet been successfully used as components of responsive molecular brushes chiefly because their well-controlled polymerization is still challenging.

Poly(4-vinylpyridine), P4VP is an example of a pH-responsive polymer. The nucleophilic nitrogen atoms can participate in reactions such as quaternization, protonation or complexation with metals. As a consequence, the applications of P4VP as ion-exchange resins [68], molecular imprinting templates or materials for membranes were reported. Linear P4VP was successfully synthesized by living anionic polymerization [69], nitroxide-mediated polymerization [70–72] NMP, ATRP [73–76], and reversible addition-fragmentation chain transfer polymerization [77] RAFT. CRP methods were also used for surface-initiated polymerization of 4VP [78–81]. There are no reports on the synthesis of 4VP-based molecular brushes but Schmidt et al. synthesized core–shell cylindrical brushes consisting of 2-vinylpyridine and styrene by polymerization of methacryloyl end-functionalized block macromonomers [10].

In this study, polymer brushes with P4VP side chains were prepared by ATRP. The appropriate catalyst and initiator selection was critical for the preparation of soluble brushes. The responsive behavior of the brushes in aqueous media was demonstrated.

2. Experimental

2.1. Materials

The monomer, 4VP, was distilled prior to use. The macroinitiator, poly(ethylene oxide) methyl ether 2-bromoisobutyrate (MePEOBiB; *MW* = 699 g/mol), was prepared by a literature procedure [82]. Poly(2-(trimethylsilyloxy)ethyl methacrylate) (P(HEMA-TMS)) and poly(2-(2-bromopropionyloxy)ethyl methacrylate) (PBPEM, M_n = 157,300 g/mol, M_w/M_n = 1.20) were prepared as previously reported [49]. Tris(2-pyridylmethyl)amine (TPMA) (>98%) was purchased from ATRP Solutions, Inc. All other reagents (Aldrich) were used as received.

2.2. Analyses

Monomer conversion was determined by gravimetry (synthesis of polymer brushes) or by NMR (synthesis of linear polymers). To determine molecular weights, polymer samples were dissolved in 50 mM solution of LiBr in DMF, containing a small amount of toluene or diphenyl ether as elution volume marker, and analyzed by size exclusion chromatography (SEC). SEC measurements were conducted using 50 mM solution of LiBr in DMF as the eluent (flow rate 1 mL/min, 50 °C), with a series of three Styrogel columns (10^5 Å, 10^3 Å, 100 Å; Polymer Standard Services) and a Waters 2410 differential refractometer. Polystyrene standards were used for the calibration. ^{1}H NMR spectra were collected on a Bruker instrument operating at 300 MHz in $CDCl_3$ or DMF-d_7 using TMS as the reference. Hydrodynamic diameters (D_H) were determined by dynamic light scattering (DLS) in DMF or aqueous solution of hydrochloric acid of varied concentrations. Solution of polymer with concentration of 1 g/L was prepared by dissolution of 10 mg of brush polymer in 10 mL of diluted HCl at concentration of 10 mM, 1 mM and 0.1 mM, respectively, and stirred overnight prior the measurement. The measurements (three per sample and averaging the results) were performed at room temperature (25 °C) with a Malvern HPP5001 High Performance Particle Sizer.

2.3. Kinetic measurements and syntheses

2.3.1. Pyridinolysis of 1-phenylethyl halides (1-PhEtX; X = Br, Cl) in DMF-d_7

To an NMR tube were added 1-PhEtX (2×10^{-4} mol, i.e., 27.4 μL of 1-PhEtBr or 26.5 μL of 1-PhEtCl) and DMF-d_7 containing TMS (0.5 mL). Pyridine-d_5 (2.5×10^{-3} mol; 0.2 mL) was added prior to the experiment and the reaction time was monitored from this moment. The tube was inserted in the NMR spectrometer (temperature 27 °C) and proton spectra were periodically acquired. Each spectrum consisted of 16 scans, which were collected over ca. 100 s, the middle of which corresponds to the reported reaction time for each kinetic point. While not inside the spectrometer, the tubes were kept in a water bath thermostated at 27 °C.

2.3.2. ATRP of 4VP in DMF

A mixture of DMF (3 mL) and 4VP (3 mL, 28 mmol) was degassed by 10 freeze–pump-thaw cycles, the mixture was frozen in liquid nitrogen, and the flask was filled with nitrogen. The flask was opened and a mixture of TPMA (0.0848 g, 0.292 mmol), CuCl (0.0192 g, 0.194 mmol), and $CuCl_2$ (0.0133 g, 0.098 mmol) was added. The flask was quickly closed with a rubber septum, evacuated and back-filled with nitrogen several times. The mixture was then allowed to thaw in a water bath thermostated at 30 °C, and the nitrogen-purged initiator, MePEOBiB of *MW* = 699 g/mol (0.16 mL) was injected. Samples were periodically withdrawn with a nitrogen-purged syringe and the reaction was eventually stopped by exposing the reaction mixture to air.

2.3.3. ATRP of 4VP from PBPEM macroinitiator, P(BPEM-graft-4VP)

PBPEM (0.100 g, 0.377 mmol initiating sites), $CuCl_2$ (0.0304 g, 0.226 mmol), TPMA (0.1284 g, 0.452 mmol), 4VP (7.9 g, 75.5 mmol), and DMF (15.5 mL) were added to a 25-mL Schlenk flask equipped with a magnetic stir bar. The flask was sealed, and the resulting solution was