Materials Science and Engineering C 29 (2009) 1604–1608

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Reverse ATRP of 4-vinylpyridine with Diethyl 2,3-Dicyano-2,3-Diphenylsuccinate/$CuCl_2$/5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclotetradecane

Hou Chen *, Ying Liang, Yangfeng Meng, Lixia Yang, Lingfang Chen, Lichun Chen, Yuan Niu

School of Chemistry and Materials Science, Ludong University, Yantai 264025, China

ARTICLE INFO

Article history:
Received 9 September 2008
Received in revised form 3 November 2008
Accepted 16 December 2008
Available online 25 December 2008

Keywords:
Reverse atom transfer radical polymerization
Block copolymers
Living polymerization
4-Vinylpyridine

ABSTRACT

Diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS) was applied to initiate reverse atom transfer radical polymerization of 4-vinylpyridine (VP) in 2-propanol with $CuCl_2$ and 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclotetradecane (Me_6[14]aneN_4) as catalyst and ligand for the first time. First-order kinetics of the polymerization rate with respect to the monomer concentration, linear increase of the molecular weight with monomer conversion and a polydispersity index in the range of 1.15–1.28 were indicatives of controlled radical polymerization. Use of Me_6[14]aneN_4 as the ligand had many advantages over the use of hexamethyl tris[2-(dimethylamino)ethyl]amine (Me_6-TREN) and 2,2′-bipyridine (bpy). A slower polymerization rate and a broad polydispersity index were observed using $CuBr_2$ instead of $CuCl_2$ as catalyst. The block copolymer PVP-b-PAN was obtained via a conventional ATRP process in *N*, *N*-dimethylformamide (DMF) using the resulting poly (4-vinylpyridine) as macroinitiator.

1. Introduction

Synthesis of well-defined polymers with predefined molecular weight, narrow molecular weight distribution, and high degree of chain end functionalization has long been of great interest in polymer chemistry. Living polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination [1,2]. Living anionic and cationic polymerizations have been widely used in the preparation of a multitude of polymer materials. However, these techniques often suffer from several drawbacks, including the limited choice of monomers and solvents and high sensitivity to moisture and carbon dioxide [3,4]. Therefore the controlled radical polymerization is becoming increasingly important, as it combines the merits of conventional radical polymerizations with the ability to give polymers with predictable molecular weight, narrow polydispersity and well-defined architecture. Atom transfer radical polymerization (ATRP) is one of the most powerful, versatile, simple and inexpensive methods in the controlled radical polymerization. Its control is achieved by the rapid equilibration of a transition metal complex that reversibly activates a halide-capped dormant chain [5–14].

4-vinylpyridine (VP) is an interesting monomer, which is basic, nucleophilic, coordinating and pH-sensitive. Well-defined Poly(4-vinylpyridine) (PVP) and their block copolymers have attracted much interests due to their potential applications including molecular imprinting polymers [15], ion-exchange resins [16,17], bio-sorption/biosensor materials [18] and microfiltration membranes [19,20]. The homo and some block copolymerizations of VP have already been approached via ATRP by Matyjaszewski [21–23] and the other researchers [24–26].

However, transition-metal-catalyzed ATRP has two major drawbacks: toxicity of halide species RX and oxidation of catalyst M_n^t/LX by oxygen in air. To overcome these drawbacks, use of conventional radical initiators in the presence of complexes of transition metals in their higher oxidation state has been reported and referred to as reverse ATRP by Matyjaszewski [27–29] and the other researchers [30]. In the past, only two kinds of conventional initiators, such as azo- and peroxide compounds, were employed in reverse ATRP [31,32]. It is well known that decomposition of these initiators is irreversible, which leads to the concentration of primary radicals rather high, especially at the early stage of polymerization at high temperature. Development of new type initiators for reverse ATRP, using carbon–carbon bond initiator instead of azo or peroxide ones, is an essential requirement. Qin has introduced a carbon–carbon bond thermal iniferter, diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS), instead of AIBN into iron-based reverse ATRP system for styrene polymerization [33].

To the best of our knowledge, only Cohen [34] reported that reverse ATRP of VP in an aqueous/1-methyl-2-pyrrolidone mixture through the use of a 2,2′-azobis(2,4-dimethylpentanitrile) initiator and a $CuCl_2$/2,2′-bipyridine catalyst-ligand complex.

Pyridine-coordinated copper complexes are not effective catalyst for ATRP, because there are significant complexing behavior of the pyridine rings of both monomer and polymer with the used copper catalyst. So the ligand with high complexing constant to copper is very necessary. Matyjaszewski [21] proposed that the multidentate ligand hexamethyl tris[2-(dimethylamino)ethyl]amine (Me_6-TREN) can

---

* Corresponding author. Tel.: +86 535 6697933; fax: +86 535 6697667.
E-mail address: sdchenhou@hotmail.com (H. Chen).

0928-4931/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.msec.2008.12.020

compete with the pyridine units to complex copper catalyst. But Me_6-TREN is not synthesized easily and has high price. Wang [26] firstly selected a macrocyclotetraamine, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclotetradecane ($Me_6[14]aneN_4$) as ligand in ATRP of VP. GPC and NMR studies showed that the molecular weight of the resulting PVP increased linearly with the conversion.

A detailed study for the optimization of the reaction conditions to prepare PVP by reverse ATRP was the starting point of this original research. Keeping all these points in mind, DCDPS was chosen to be the initiator, $Me_6[14]aneN_4$ was selected to be the ligand and 2-propanol was used as the solvent. The successful approach of the well-controlled reverse ATRP of VP with a new $CuCl_2/Me_6[14]aneN_4$ catalyst system by using DCDPS as the initiator in 2-propanol was described for the first time. Effects of different ligand, copper halides and solvents on the polymerization were investigated. Block polymerization of acrylonitrtile (AN) via ATRP in *N*, *N*-dimethylformamide (DMF) using PVP as macroinitiator was also attempted.

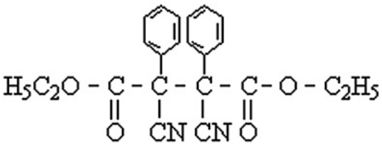
2. Experimental

2.1. Reagents

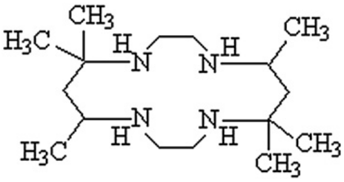
VP (Acros, 96%) was dried over CaH_2 and distilled under reduced pressure just before polymerization. Anhydrous $CuCl_2$ (Shanghai Chemical Reagents Co., A. R. grade) was dried under vacuum at 60 °C before use. DCDPS (Structure 1) was prepared according to the method reported previously [35]. ^1H NMR (δ, ppm, in $CDCl_3$, 300 MHz): 1.24 [6H, $-CH_2CH_3$], 4.28 [4H, CH_2CH_3], 7.41 [10H, C_6H_5-]. Scheme 1 shows the chemical structure of DCDPS. $Me_6[14]aneN_4$ was prepared according to the literature [36]. Scheme 2 shows the chemical structure of $Me_6[14]aneN_4$. Me_6-TREN was synthesized from tris(2-(aminoethyl)amine according to the literature [37,38]. Scheme 3 shows the chemical structure of Me_6-TREN. 2,2′-bipyridine(bpy, Shanghai Chemical Reagents, A. R.grade) was recrystallized from acetone. 2-propanol (Tianjin Ruijinte Chemical Reagents Co., A. R. grade) was used as received. *N*, *N*-dimethylformamide (DMF, Shanghai Dongyi Chemical Reagents Co.) was distilled at reduced pressure and stored over type4-Å molecular sieves before use.

2.2. Polymerization

A typical example of the general procedure was as follows. A dry flask was filled with the reagents in the order of 2-propanol, $Me_6[14]aneN_4$, $CuCl_2$, DCDPS and VP. It was degassed and charged with N_2 (3 times). The mixture was sealed under N_2 and stirred at room temperature until the catalyst was dissolved. The flask was then immersed in an oil bath at the desired temperature detected by a thermostat. After the reaction was carried out for a prescribed time, the flask was rapidly cooled down in ice water. A small amount of sample was taken out and the monomer conversion was determined based on based on ^1H NMR data. The residual resultant mixture was then dissolved in 2-propanol, and the solution was passed through a short alumina column for removal of the copper complexes. A rotary evaporator was employed to concentrate the eluent solution, and then precipitate was obtained by pouring residual liquid into a large amount of diethyl ether. Finally the products were filtered several times and dried at 50 °C under vacuum.



Scheme 1. Chemical structure of DCDPS.



Scheme 2. Chemical structure of Me_6[14]$aneN_4$.

2.3. Characterization

The molecular weight (M_n) and polydispersity index (PDI) of PVP were measured by gel permeation chromatography (GPC). GPC was performed with a Waters 1515 solvent delivery system (Milford, MA) at a flow rate of 1.0 $mL\cdot min^{-1}$ through a combination of Waters HT3, HT4, and HT5 styragel columns. Poly(methyl methacrylate) standards were used to calibrate the columns. The analysis was undertaken at 35 °C with purified high-performance-liquid-chromatography-grade DMF as an eluent. A Waters 2414 differential refractometer was used as the detector.

According to the characteristics of living polymerization, the theoretical molecular weight (M_{th}) could be calculated from the following Eq. (1) [39]:

$$M_{th} = \frac{[4VP]}{2[DCDPS]} \times M_{w4VP} \times \text{Conversion} \tag{1}$$

where M_{WVP} is the molecular weight of VP.

The conversion of the monomer was determined based on ^1H NMR data and calculated according to the Eq. (2):

$$\text{Conversion}(\%) = \frac{I_{8.4} - I_{5.8}}{I_{8.4}} \times 100\% \tag{2}$$

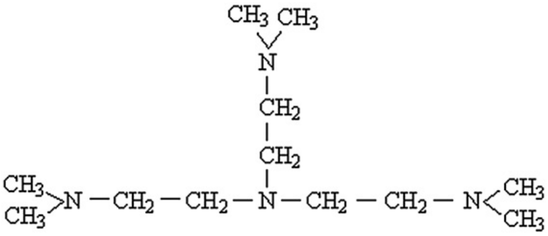
where $I_{8.4}$ and $I_{5.8}$ are the integral values of the peaks at $\delta = 8.4$ and 5.5–6.0, respectively. ^1H NMR spectra were recorded on a Bruker Avance300 NMR spectrometer, using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal reference.

Infrared spectroscopy and elemental analysis were employed to confirm the successful synthesis of PVP-b-PAN. Infrared spectra of PVP-b-PAN were obtained on a Nicolet MAGNA IR 550 (series II) spectrophotometer using KBr pellets in the 400–4000 cm^{-1} region with a resolution of 4 cm^{-1}, by accumulating 32 scans. C, N analysis of PVP-b-PAN were subjected to elemental analysis by the Elementar VarioEL III instrument (Elementar Co., Germany).

3. Results and discussion

3.1. Reverse ATRP of VP

Reverse ATRP of VP was carried out in 2-propanol with DCDPS as initiator and $CuCl_2/Me_6[14]aneN_4$ as catalyst complex. A plot of ln $[M]_0/[M]$ versus time was shown in Fig. 1, a straight line was observed. The linearity of the plot indicated that the polymerization was approximately first-order with respect to the monomer concentration.



Scheme 3. Chemical structure of Me_6-TREN.