Nitroxide polymer brushes prepared by surface-initiated ARGET ATRP and their selective oxidation performances

S. J. Liu^{1,2*}, Q. Q. Hu¹, F. Q. Zhao^{1,2}, X. M. Chu¹, P. X. Li¹, E. J. Tang¹

¹College of Chemical & Pharmaceutical Engineering, Hebei University of Science and Technology, 050018 Shijiazhuang, PR China

²Hebei Provincial Engineering and Technology Research Center of Solid Waste Utilization, 050018 Shijiazhuang, PR China

Received 3 April 2014; accepted in revised form 18 June 2014

Abstract. Polymer brushes with 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TMPM) units, grafted on the cross-linked polystyrene (PS) microspheres, were synthesized *via* surface-initiated ARGET (activators regenerated by electron transfer) ATRP (atom transfer radical polymerization). They were further oxidized to yield nitroxide polymer brushes containing nitroxide radical units (TEMPO). The obtained polymer brushes were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron spin resonance (ESR) and gel permeation chromatography (GPC). The catalytic properties of nitroxide polymer brushes for selective oxidation of benzyl alcohol were investigated. The results showed that the performances were good and the yield was up to 96%. Furthermore, the block brush had similar catalyst properties to non-supported TEMPO in terms of activity and selectivity. It could be recovered by centrifugation. The unity of high catalyst property and easy recovery was achieved.

Keywords: tailor-made polymers, nitroxide polymer brushes, selective oxidation, ARGET ATRP

1. Introduction

Poly(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl methacrylate) (PTMA) is a kind of promising cathode-active materials for organic radical batteries [1–5]. It is a polymer containing methacrylate backbone grafted with 2, 2, 6, 6-tetramethylpiperidin-1-oxyl-4-yl (TEMPO). TEMPO is a stable nitroxide radical. In order to prevent the nitroxide radical polymer dissolving into the electrolytes, Lee and coworkers [3–5] synthesized nitroxide polymer brushes which the PTMA was grafted onto the surface of silica, indium tin oxide and other substrates *via* surface-initiated ATRP, and the electrochemical properties were improved.

Besides, TEMPO is a good catalyst for catalytic selective oxidation of alcohol. However, the price of TEMPO is high, and its residue in the final prod-

ucts may affect the product purity. In the laboratory, product can be purified by column chromatography. However, the implementation is difficult in large-scale industrial production. So measures should be taken to make TEMPO recycled. To solve this problem, TEMPO has been immobilized onto inorganic (such as silica, activated carbon, molecular sieve and aluminum oxide) and organic supports (such as polymers and ionic liquids) affording solid catalysts, which are readily separated from the reaction mixtures. Using polymer as carrier, the grafting of TEMPO was easy, and some supported TEMPO showed new catalytic features compared with the non-supported TEMPO [6–16]. However, these polymer supports had, in general, a detrimental effect on the rates of reaction when compared to unsupported species. Furthermore, the supported amounts and

*Corresponding author, e-mail: sjliu16@163.com

location were also difficult to control. While the PTMA brush with TEMPO groups, it can be seen as a polymer brush supported TEMPO catalyst system. With the help of special designed brush structure and preparation method, the above problems may be solved.

Compared with the traditional ATRP method, ARGET ATRP uses significantly reduced copper catalyst concentration (down to ppm levels) and also imparts a degree of oxygen tolerance to the reaction [17]. These advantages make it a potentially more industrially attractive technique. ARGET ATRP has proven to be a very efficient tool in the preparation of polymer brushes. The used substrates include cellulose [18], polymer microspheres [19], silica [20], carbon nanotubes [21], etc. The used monomers include methyl methacrylate (MMA), styrene (St), methyl glycidyl ester of acrylic (GMA), etc. Recently, synthesis of tert-butyl methacrylate/2-(dimethylamino ethyl) methacrylate based densely grafted brushes by ATRP/ARGET ATRP was reported by Gromadzki *et al.* [22]. Stimuli-responsive poly-ampholyte brushes were obtained by quantitative hydrolysis of tert-butyl methacrylate units. To the best of our knowledge, grafting nitroxide polymer brushes on cross-linked PS microspheres *via* ARGET ATRP and using them as catalysts for selective oxidation of alcohols have not yet been reported.

In this paper, polymer brushes with TPMU units on the cross-linked PS microspheres, were synthesized *via* surface-initiated ARGET ATRP. Then piperidyl was oxidized by *m*-chloroperoxybenzoic acid (mCPBA) into nitroxide radical. The nitroxide polymer brushes were produced. These nitroxide polymer brushes were used as catalysts for selective oxidation of benzyl alcohol. With the insolubility of cross-linked PS microsphere matrix and the solubility of linear nitroxide polymer brushes, the high catalytic property and easy recovery performance were achieved.

2. Materials and methods

2.1. Materials

α -Bromoisobutyryl bromide (98%), copper (II) bromide (CuBr_2 , 99%), Tin(II) 2-ethylhexanoate (Sn(EH)_2 , 95%) and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%), were obtained from Aladdin Industrial Corporation (Shanghai, China) and used as received. *m*-Chloroperoxybenzoic acid (mCPBA, 75%) purchased from J&K

Chemical (Beijing, China) was recrystallized in methanol before use. 2,2,6,6-Tetramethyl-4-piperidyl methacrylate (TPM, 98%) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Other monomers including styrene (St, 99%), divinylbenzene (DVB, 55%), hydroxyethyl methacrylate (HEMA, 96%) and methyl methacrylate (MMA, 99%) were offered by Aladdin Industrial Corporation (Shanghai, China). These monomers were passed through a column of neutral aluminum oxide prior to use to remove the inhibitor. Other reagents were from Sinopharm Chemical Reagent Company (China) and used without further purification.

2.2. Synthesis of nitroxide polymer brushes on cross-linked PS microspheres

In this study, we prepared two nitroxide polymer brushes: the homopolymer brush of PTMA and the block polymer brush of P(MMA-*b*-TMA). The preparation process of P(MMA-*b*-TMA) brush was illustrated in Figure 1.

Figure 1. Synthesis of P(MMA-*b*-TMA) brushes on PS microspheres

2.2.1. Preparation of cross-linked P(St-co-HEMA) microspheres by soap-free emulsion polymerization

The cross-linked P(St-co-HEMA) microspheres were prepared by a soap-free emulsion polymerization in a 1000 mL round-bottom flask equipped with a mechanical stirrer and reflux condenser at N₂ atmosphere. 27 g St, 1.3 g DVB, 0.054 g NaOH, 0.054 g NaHCO₃ and 500 mL distilled water were

added to the reactor. When the temperature rose to 75°C, initiator solutions (0.5 g potassium persulfate dissolved in 40 mL water) was added to initiate the polymerization. 2.7 g HEMA was added 5 hours later. After 3 hours' polymerization, the cross-linked P(St-co-HEMA) microspheres were obtained by centrifuging and drying.

2.2.2. Immobilization of ATRP initiator on cross-linked P(St-co-HEMA) microspheres

In an ice bath, α -bromoisobutyryl bromide (1.8 g, 8 mmol) was added to a dispersion of microspheres (5 g) and triethylamine (0.9 g, 9 mmol) in CH_2Cl_2 (100 mL). The reaction was quenched by the addition of methanol after 5 hours of gentle stirring at ambient temperature. The microspheres were centrifuged, washed with CH_2Cl_2 , methanol and dried at ambient conditions.

2.2.3. Synthesis of PTMPM brush via surface-initiated ARGET ATRP

In nitrogen atmosphere, anisole (30 mL) and TMPM (5 g, 22.2 mmol) were added to a 50 mL three-necked flask. After TMPM was dissolved, added CuBr_2 (4.5 mg, 0.02 mmol) and PMDETA (0.083 mL, 0.4 mmol) at 40°C. Then the macromolecular initiator (1.25 g, containing 0.4 mmol Br) was added. When the system completely decentralized and the temperature rose to 80°C, $\text{Sn}(\text{EH})_2$ (0.13 mL, 0.4 mmol) was added to initiate the reaction. After 105 min, the polymerization was stopped by exposing the solution to air. The PTMPM brush was obtained by centrifugation, washing with anisole, and dried in a vacuum oven at 60°C to constant weight.

The synthesis of block copolymer brush of P(MMA-b-TMPM) was similar to the above process. Firstly PMMA brush was prepared, and then P(MMA-b-TMPM) block brush was obtained through using PMMA brush as the macromolecular initiator and TMPM as the monomer.

2.2.4. Synthesis of nitroxide polymer brushes

PTMPM brush (1.654 g) was dispersed in 60 mL of CH_2Cl_2 . Then, 20 mL CH_2Cl_2 solution of mCPBA (1 g, 5.9 mmol) was dropped at 0°C. After 1 h, the mixture was poured into 120 mL n-hexane, and the orange precipitate appeared. Then the pink solid product was washed and ultrasonicated again with

dimethyl formamide (DMF) three times and dried in a vacuum oven for 24 hours at 60°C to give PTMA brush. With similar process, the P(MMA-b-TMA) brush was obtained.

2.2.5. Basic hydrolysis of polymer brush

50 mL of a 1 M KOH/ethanol solution was added to 100 mg of polymer brush in 200 mL of tetrahydrofuran (THF). The mixture was refluxed at 80°C for 72 hrs, followed by filtration and then redissolved into THF. The resultant polymer was precipitated by the addition of acidified methanol.

2.2.6. Characterization of polymer brushes

The particle size of polymer microsphere was measured by laser particle size analyzer (Zetasizer Malvern Nano S90, Malvern Instruments Ltd, United Kingdom). The Br content of macromolecular initiator was estimated by Automatic Elemental Analyzer (Chncorder-MF-3, United States). The monomer conversion of polymerization was given by gravimetry method. The morphology of polymer brush was characterized by using TEM (Jeol 100CX-II, Jeol Co., Japan) and SEM (S-4800-I, HITACHI, Japan). After polymer brushes cut from the substrate surface by hydrolysis, the number molecular weight (M_n) and dispersity index (D) were determined using THF (0.8 mL/min) as the mobile phase at 45°C by GPC (Waters GPCV 2000 with a combined refractive index and viscosity detector, United States). A universal calibration method was performed using series of narrow linear polystyrene standards. Conversion of PTMA brush from PTMPM brush was estimated by electron spin resonance (ESR, Bruker EMX-10, United States) [3].

2.3. General process for benzyl alcohol oxidation

8.6 mL of NaClO aqueous solution ($0.121 \text{ g} \cdot \text{mL}^{-1}$) and 8.6 mL of NaHCO_3 aqueous solution ($0.05 \text{ g} \cdot \text{mL}^{-1}$) were added to a solution of benzyl alcohol (1.2 mL, 11.5 mmol) in 10 g of CH_2Cl_2 containing 1% mol of polymer brush supported TEMPO [PTMA 0.091 g or P(MMA-b-TMA) 0.065 g] and 10% mol of KBr (0.137 g, 1.15 mmol). The reaction mixture was stirred at 0°C for 3 mins. Then, $\text{Na}_2\text{S}_2\text{O}_3$ was added to stop the reaction. The organic phase was separated, dried over MgSO_4 , and finally analyzed by gas chromatography (GC). The process was illustrated in Figure 2.

Figure 2. Oxidation of benzyl alcohol by the nitroxide polymer brush

2.4. General procedure for the recovery of P(MMA-b-TMA) brush

The P(MMA-b-TMA) brush was retrieved and circulated use. The brushes in aqueous phase were deposited by filtration, washing with DMF and drying. Repeated the above operation (see section 2.3) 5 times to study the catalytic properties of recycled brushes.

3. Results and discussion

3.1. Synthesis of cross-linked PS microspheres with ATRP initiator

The cross-linked surface-hydroxylated PS microspheres, P(St-co-HEMA), were prepared by soap-free emulsion polymerization. From the SEM image in Figure 3a, it was seen that P(St-co-HEMA) had the particle size of about 400 nm, in accordance with the dynamic light scattering result (425 nm). Through the O-acylation reaction of the surface hydroxyl groups of P(St-co-HEMA) with α -bromoisobutyryl bromide, the ATRP initiator was immobilized. The content of Br in these particles was about 0.32 mmol/g, which was estimated by the elemental analysis result. These microspheres were used as macromolecular initiators to prepare polymer brushes.

3.2. Synthesis of nitroxide polymer brushes

3.2.1. Homopolymer brush of PTMPM

The PTMPM brush was prepared by surface-initiated ARGET ATRP. The SEM image (Figure 3b)

showed that PTMPM brushes/PS nanoparticles had a slight adhesion due to the presence of polymer brushes. Similar phenomenon was reported by Lin *et al.* [3] when they grafted nitroxide polymer brushes on silica nanoparticles. Its FT-IR spectrum (ATR, cm^{-1}) could be seen in Figure 4: 972 (m), 1152 (vs, vas (OCC=O)), 1236 (s, vas (CC=O)), 1378 (m, δ s (CH₃)), 1452 (m, d (CH₂)), 1724 (vs, v (C=O)), 2960 (m, v(CH)), 3332 (m), 3423 (m, v (NH)). TEM images (Figure 5a, 5b) indicated that the brushes showed a core-shell structure. The core was PS matrix with a diameter of about 400 nm and the shell was a layer of TMPM polymer chains. Particle size of PTMPM homopolymer brush was about 500 nm. The adhesion among the particles may be caused by the intertwining of brushes. Therefore, the PTMPM brush was successfully prepared.

Grafting density (chains nm^{-2}) of polymer brush was calculated according to the Equation (1):

$$\text{grafting density} = \frac{W}{M \cdot S} \cdot N_A \cdot 10^{-18} \quad (1)$$

where W was the grafting amount of polymer brush [g] polymer brush/g matrix; M was the number

Figure 4. FT-IR spectrum for PTMPM brushes/P(St-co-HEMA) microspheres

Figure 3. SEM micrographs for the bare P(St-co-HEMA) microspheres (a), PTMPM brushes/P(St-co-HEMA) microspheres (b) and P(MMA-b-TMPM) brushes/P(St-co-HEMA) microspheres (c)

Figure 5. TEM micrographs of the prepared polymer brushes: PTMPM brushes/P(St-co-HEMA) microspheres, (a) and (b); P(MMA-b-TMPM) brushes/P(St-co-HEMA) microspheres, (c) and (d)

average molecular weight of the polymer brush [g/mol]. S was the specific surface area [$\text{m}^2 \cdot \text{g}^{-1}$]. N_A was Avogadro's number.

For the PTMPM brush, the grafting amount was 0.75 g TMPM brush/g substrate. Brushes were cut down from PS matrix by hydrolysis. It was measured that $M_n = 16\,000$ g/mol and dispersity index (D) = 1.25. The grafting density was about $3.3 \text{ chains nm}^{-2}$. This grafting density was higher than that on silica nanoparticles, which was about 1 chains nm^{-2} [3].

3.2.2. Block copolymer brush of P(MMA-b-TMPM)

The block copolymer brush of P(MMA-b-TMPM) was synthesized with the process as shown in Figure 1. From the SEM micrograph in Figure 3c, particles with P(MMA-b-TMPM) brushes had an irregular shape and were non-spherical. The long brushes may be intertwined with each other. It was seen from the TEM images (Figure 5c, 5d) that, the particles with block brushes also showed a core-shell structure.

The grafting amount of block copolymer brush of P(MMA-b-TMPM) was 0.69 g TMPM brush/g sub-

strate. Its M_n was 22 000 g/mol and D was 1.41. The grafting density was about $3.8 \text{ chains nm}^{-2}$.

3.2.3. Preparation of nitroxide polymer brushes

The piperidyl groups of PTMPM and P(MMA-b-TMPM) brushes were oxidized by mCPBA into nitroxide radical, and two nitroxide polymer brushes (PTMA and P(MMA-b-TMA)) were obtained.

Because FT-IR spectra of PTMA was similar with PTMPM (the absorption peak of N–O· was very weak) [3], so the spectrum could not be used to judge whether the reaction occurred. But during the course of the experiment, the phenomenon was obvious that the system changed from white to orange. The commercial TEMPO was orange. Furthermore, the conversion for TEMPO of the nitroxide polymer brushes were measured by ESR [3]. The conversion was about 95% after the oxidation. The nitroxide polymer brushes prepared in this work showed a high level of TEMPO immobilization, $3.1 \text{ mmol} \cdot \text{g}^{-1}$ for PTMA and $3.6 \text{ mmol} \cdot \text{g}^{-1}$ for P(MMA-b-TMA). This density level is considerably higher than that of the TEMPO polymer grafted on silica (up to $2.1 \text{ mmol} \cdot \text{g}^{-1}$) [23].

3.3. The performance of nitroxide polymer brushes for catalytic oxidation of benzyl alcohol

With NaClO as the oxidant, the nitroxide polymer brushes as catalysts, benzyl alcohol was selectively oxidized to benzaldehyde. The catalyst performance of nitroxide polymer brushes was compared with non-supported TEMPO. GC results showed that the system possessed excellent selectivity using non-supported TEMPO, PTMA brush and P(MMA-b-TMA) brush as catalysts. No characteristic peaks of benzoic acid were found. The yield of benzaldehyde was, 95, 91 and 96%, respectively. Block copolymer brush of P(MMA-b-TMA) had similar results with non-supported TEMPO. It may be that the special structure of block brushes made TEMPO groups mainly distributed in the outer of particles, which was helpful to fully contact with the reactants.

Recycling performance of the P(MMA-b-TMA) brush was investigated after the filtration recovery. The yield results for 5 cycles, were shown in Figure 6. It was found that the yield did not fall significantly after 5 cycles. Furthermore, benzoic acid was not detected. The high catalytic activities and preservation of activity upon recycling of these brushes may be attributed to enhanced regeneration of the nitroxyl species as a result of intramolecular synproportionation [10]. The oxidation for other primary alcohols and secondary alcohols is under work.

Figure 6. Recyclability of P(MMA-b-TMA) brushes in the oxidation of benzyl alcohol to benzaldehyde

4. Conclusions

The surface-hydroxylated cross-linked PS microspheres were prepared by soap-free emulsion poly-

merization, and then ATRP initiator was supported on them. Using these microspheres as macromolecular initiators, the homopolymer brush of PTMPM and block copolymer brush of P(MMA-b-TMPM) were synthesized *via* surface-initiated ARGET ATRP, and the grafting density was 3.3 and 3.8 chains nm⁻² respectively. PTMPM and P(MMA-b-TMPM) brushes were further oxidized by mCPBA to yield nitroxide polymer brushes of PTMA and P(MMA-b-TMA) with TEMPO groups. With NaClO as oxidant, selective oxidation of benzyl alcohol to benzaldehyde as template reaction, the catalytic performances of nitroxide polymer brushes were studied. The results showed that the brushes had excellent catalytic properties, and the P(MMA-b-TMA) brush demonstrated an equivalent catalytic performance with the non-supported TEMPO. The catalyst system was easy to recycle, and the yield did not fall significantly after 5 cycles.

Acknowledgements

This study was supported by Natural Science Foundation of China (NO. 21304030), Natural Science Foundation of Hebei Province (NO. B2012208017) and Outstanding Youth Fund in Hebei Province Department of Education (NO. YQ2013001). Here we expressed the heartfelt thanks for the support.

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