Platinum Atoms Dispersed in Single-chain Polymer Nanoparticles

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Abstract The intramolecular cross-linking of single polymer chains can form single-chain nanoparticles (SCNPs), which have many applications. In this study, styrenic copolymers with pendant triphenylphosphine as the coordination site for platinum ions (Pt(II)) and benzocyclobutene as the latent reactive groups are synthesized. Triphenylphosphine groups in the chains can coordinate Pt(II) and aid slight single-chain folding in dilute solution. The intramolecular cross-linking caused by the ring-open reaction of benzocyclobutene completes the single-chain collapse and forms stable SCNPs in dilute solution. Pt(II) embedded in SCNPs can be further reduced to platinum atoms (Pt(0)). Pt(0) steadily and atomically dispersed in SCNPs exhibits better catalytic properties than normal polymer carried platinum particles do for the reduction of \( p \)-nitrophenol to \( p \)-aminophenol.

Keywords Single-chain; Polymer nanoparticles; Intramolecular cross-linking; Platinum; Coordination

INTRODUCTION

The preparation of polymer nanoparticles with a controlled size and pre-determined arrangement of functional groups is an important area, which is driven by the use of these tailor-made, functional nanoparticles in a variety of applications.\cite{1-3} The intramolecular collapse of single polymer chains assisted by intramolecular cross-linking can form single-chain nanoparticles (SCNPs), which can be widely used in many fields such as electronics,\cite{4,5} catalysts,\cite{6,7} nanomedicines,\cite{8,9} and so on. The intramolecular cross-linking can be classified into irreversible covalent bonding,\cite{10,11} dynamic covalent bonding,\cite{12,13} and noncovalent interaction.\cite{14,15} Many studies have reported the strategies involving the intramolecular coupling of single-chain polymer nanoparticles comprised of two steps.\cite{16} In simple terms, the first step contains the synthesis of cross-linkable linear polymers\cite{17} and the second involves the preparation of single-chain nanoparticles in ultra-dilute solution.\cite{18,19} Compared with inorganic nanoparticles which depend on the environmental condition or the designed template,\cite{20} SCNPs rely on the molecular weight and content of intramolecular cross-linking groups, which can be held steady in the polymerization.\cite{21,22} Consequently, various SCNPs with different functions can be obtained via combining diverse functional monomers and cross-linkable monomers.\cite{23} Furthermore, this method can prepare polymeric nanoparticles in 5–20 nm diameters via controlling intramolecular coupling, folding, and collapsing of single polymer chains.\cite{24,25}

Among various noncovalent interactions to prepare SCNPs, the metal ion-ligand interaction is a useful method for helping the single-chain folding and forming SCNPs.\cite{26,27} SCNPs internally form the reticular structure by a good supply of cross-linking.\cite{28} Cross-linked by metal ion-ligand interaction, SCNPs with the metal ions still have the catalytic performance,\cite{29} which means that the inner space of SCNPs is not fully enclosed and the reactants can contact the metal ions. Thus, it is possible to reduce these ions into metal atoms which can be embedded in SCNPs as the catalyst. However, the metal ion-ligand interaction may be destroyed and SCNPs will lose the stability after the reduction of the metal ions. To physically embed these reduced metal atoms in SCNPs and regulate the reticular structure, the further covalent intramolecular cross-linking of SCNPs is necessary. The state of the atomically dispersed metal atoms in SCNPs relies on the reticular structure of SCNPs to embed and stabilize these atoms (single atoms, clusters, or other aggregates of atoms).

In present study, the linear polymer was folded twice by platinum ion coordination and covalent cross-linking to obtain SCNPs with stable and suitable reticular structure, and the degree of the second collapse can be positively correlated with the degree of cross-linking. After the composite SCNPs are reduced, the platinum ions coordinated in SCNPs can be reduced to platinum atoms and embedded in the reticular structure of covalently cross-linked SCNPs, which may exhibit better catalytic performance due to the possible existence of platinum clusters or even single platinum atoms.

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EXPERIMENTAL

Materials

4-Diphenylphosphino styrene (97%, Aldrich), styrene (CP, containing 10–15 ppm 4-tert-butylcatechol stabilizer), dichloro-(1,5-cyclooctadiene) platinum(II) (98%, Pt 51.6%–52.6%), 4-vinylbenzocyclobutene (98%), methanol (99.9%), dichloromethane (99.9%, extra dry, with molecular sieves, water ≤ 30 ppm) (by K.F.), dibenzyl ether (95%), and ethanol (99.5%, extra dry, with molecular sieves, Energy Seal) were purchased from Energy Chemical Co. Sodium borohydride (99%) and toluene (99.0%) were purchased from Sinopharm Chemical Reagent Co. Styrene and 4-vinylbenzocyclobutene were treated with a neutral alumina column before using. Other chemicals were used as received.

Synthesis of P(St-co-PPh-co-BCB)

Poly(styrene-co-(4-diphenylphosphino styrene)-co-4-vinylbenzocyclobutene) (P(St-co-PPh-co-BCB)) was synthesized via free radical polymerization. Styrene (1.25 g, 12 mmol), 4-diphenylphosphino styrene (1.153 g/0.577 g/0.288 g, 4 mmol/2 mmol/1 mmol), 4-vinylbenzocyclobutene (0.521 g, 4 mmol), azobisobutyronitrile (AIBN) (0.032 g, 0.2 mmol), and dry toluene (12 mL) were added into a dried three-necked flask. After oxidation by 3 cycles of freeze-pump-thaw, the reaction was carried out at 80 °C for 2 h. The solution was cooled to room temperature after the reaction. Then 5 mL of tetrahydrofuran (THF) was added into the flask and the colorless solution was precipitated in cold methanol. The dissolution-precipitation process was repeated 3 times to purify the product. The final product was filtered and dried in a vacuum oven at 50 °C, whereby a white powder was obtained.

Preparation of SCNPs-Pt(II)

P(St-co-PPh-co-BCB) (0.5 g) (0.43 mmol triphenylphosphine) was dissolved in super dry dichloromethane (50 mL) in a 250 mL three-necked flask. Dichloro(1,5-cyclooctadiene) platinum(II) (0.16 g, 0.43 mmol) was dissolved into super dry dichloromethane (100 mL) in a three-necked flask. The solution was bubbled with dry nitrogen for 30 min to protect triphenylphosphine from oxidation. The polymer solution was added dropwise into platinum-solution (4 mL·h⁻¹) at room temperature with magnetic stirring. After the polymer dripped, the mixture was stirred continuously for 1 h. The mixture was concentrated by reduced pressure distillation. After distillation, the mixture was oily and then the solution was precipitated in cold methanol. The final product was filtered and dried in a vacuum oven at 50 °C.

Preparation of SCNPs-Pt(0)

In a 250 mL three-necked flask, NaBH₄ (0.314 g, 8.5 mmol) was dissolved into 50 mL of THF and was stirred by magnetic stirring under nitrogen atmosphere. SCNPs-Pt(III) (0.1 g, containing about 0.016 g platinum ion, 0.0855 mmol) was dissolved into 20 mL of THF and was added dropwise into NaBH₄ solution (0.5 mL·min⁻¹) at room temperature. After completion of adding SCNPs-Pt(III), the solution was continued to be stirred for 3 h. THF was removed by reduced pressure, and then the mixture was added in 20 mL deionized water. The final product was collected via centrifugation, and dried at 80 °C in a vacuum oven.

RESULTS AND DISCUSSION

Synthesis of Linear Polymers and Preparation of SCNPs-Pt(0)

The preparation of single-chain polymeric nanoparticles with Pt(0) atoms involves three steps (shown in Fig. 1). The first step is the combination of cross-linkable groups and chelating groups into linear polymer. The second step comprises trapping Pt(II) ions via chelating groups in the polymer, which also causes slight folding of the single chain in dilute solution, and then highly collapsing via intramolecular cross-linking of the single chain. Finally, the metal ions, trapped or embedded in SCNPs, were used as received.

Preparation of SCNPs-Pt(0)

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Catalysis of SCNPs-Pt(0)

To test the catalytic activity of Pt(0) carried by SCNPs, SCNPs-Pt(0) was used as the catalyst of the reduction of p-nitrophenol to p-aminophenol by NaBH₄. The concentration of p-nitrophenol was 0.06 mmol·L⁻¹ and that of NaBH₄ was 6 mmol·L⁻¹. The pH value was adjusted to 10 with NaOH solution. After mixing the solution, SCNPs-Pt(0) was added (concentration of Pt = 2 mg·L⁻¹) to motivate the reduction. The process of the reduction was monitored by measuring the extinction of solution at 400 nm as a function of time t.

Characterization

¹H-NMR measurements were carried out on Bruker 400 MHz spectrometer, CDCl₃ as the solvent. FTIR spectra were measured on Thermo Nicolet iSS spectrometer (Thermo Nicolet Co.). X-ray photoelectron spectroscopy (XPS) was measured on ESCA LAB 250Xi (Thermo Electron Co.). Gel permeation chromatography (GPC) was used to evaluate the apparent molecular weight of the samples, which was performed on 1200 Infinity Series (Agilent Technologies), with dimethyl formamide (HPLC grade) as eluent and polyethylene oxide as standard. Thermogravimetric analysis (TG) was conducted on STA 449C (NETZSCH Co.). UV-Vis spectra were recorded on a Mapada UV-6300 spectrophotometer (Shanghai Mapada Instruments Co.). Transmission electron microscopy (TEM) of the samples was performed on Hitachi H-600. The average particle size of the nanoparticles was also determined by dynamic light scattering (DLS) (Malvern Autosizer 4700), equipped with a solid-state laser (ILT 5500 QSL, output power 100 mW at λ = 532 nm) as light source. The solution was filtered through a 0.45 μm filter before the measurement.

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can be copolymerized randomly with styrene. The controlled free radical polymerization such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization can control the molecular weight distribution of polymers, which fits the synthesis of polystyrene and the polymer with similar structure. However, ATRP usually leads metal ions into polymers, which will influence ligand groups, while RAFT brings S or N element which can chelate metal ions into polymer.[30] BCB has an advantage in stability to radical polymerization, high reactivity at higher temperature, and no influence on chelating groups.[31] PPh$_3$ has high coordinating ability to Pt ions.[32] In present study, the common free radical polymerization was used and only azobisisobutyronitrile was used as the initiator, which insures the random copolymers containing only three monomers. There are three sections respectively expressing hydrogen of triphenylphosphine, styrene, and benzocyclobutene in NMR spectrum (Fig. 2), and the peak integration of $^1$H-NMR spectrum shows good agreements with the proposed structure. The signal at 3 ppm disappears (Fig. 3), which means the successful cross-linking of BCB, and the broad resonance at 2–3 ppm is generated by ring opening of the BCB groups and coupling to give cyclooctane derivatives according to the literatures[33,34]. Additionally, the functional groups and polymer remain stable in the synthesis process as proved by FTIR spectra (shown in Fig. S1 in the electronic supplementary information, ESI).[35]

Linear (P(St-co-PPh-co-BCB)) firstly coordinates with Pt(II) in solution to form the precursor (P(St-co-PPh-co-BCB)-Pt(II)) of the nanoparticles, in which somewhat single-chain folding exists caused by the coordination between Pt(II) and triphenylphosphine on the single polymer chain in the dilute solution. Then the precursor undergoes single-chain collapse by intramolecular cross-linking of benzocyclobutene (BCB) groups to give the single-chain nanoparticles with Pt(II) (SCNPs-Pt(II)). Pt(II) is coordinated and confined within SCNPs. The platinum atoms (Pt(0)) confined in SCNPs can be then obtained after the reduction of Pt(II). Furthermore, the nanoparticles with platinum atoms (SCNPs-Pt(0)) obtained from this method are soluble in common solvents, and atomic dispersion of Pt(0) is possibly available in SCNPs, depending on the reticular structure of SCNPs and the spacer length between two coordination sites.

**Morphology and Size Changes of Linear Polymers and SCNPs**

The data of GPC and DLS for P(St-co-PPh-co-BCB), P(St-co-PPh-co-BCB)-Pt(II), and SCNPs-Pt(II) with different contents of BCB units in the polymers are compared (shown in Table 1, Figs. S2 and S3 in ESI). Several literatures[27] have shown that the content of cross-linking units influences the size of SCNPs. It is obvious that P(St-co-PPh-co-BCB) with similar molecular weight have different diameters when they are converted into nanoparticles due to the different contents of BCB groups. As the content of BCB groups increases, the size of SCNPs-Pt(II) decreases, which indicates that the content of cross-linking groups affects the degree of collapse of polymer single chains. It can also be seen from TEM images (shown in Fig. 4 and Fig. S4 in ESI) that a similarly tapered cladding layer structure of the linear polymers was formed after coordinated with platinum ions (P(St-co-PPh-co-BCB)-Pt(II) in Fig. 4a). When P(St-co-PPh-co-BCB)-Pt(II) chains were converted into nanoparticles and Pt(II) ions were reduced, the size of SCNPs-Pt(0) in Fig. 4(b) decreases significantly. The appearance of P(St-co-PPh-co-BCB)-Pt(II) is also significantly different from that of SCNPs-Pt(0). P(St-co-PPh-co-BCB)-Pt(II) is almost colorless, while SCNPs-Pt(0) is nearly black after centrifugation. The size and size distribution of SCNPs-Pt(0) are characterized by TEM (shown in Fig. 4c). From the results of DLS and GPC, the hydrodynamic diameter of P(St-co-PPh-co-BCB)-Pt(II) is only slightly reduced than that of P(St-co-PPh-co-BCB) due to the slight intramolecular cross-linking caused by the non-cova-
lent interaction of the coordination among triphenylphosphine groups and platinum ions. From the results of TEM, DLS, and GPC, the size of the nanoparticles is much smaller than those of P(St-co-PPh-co-BCB)-Pt(II) and P(St-co-PPh-co-BCB), indicating that the main structure of the nanoparticles was well collapsed and stabilized by the intramolecular cross-linking via covalent bonds from BCB. Both Pt(II) and Pt(0) are well embedded and stabilized inside SCNPs.

**Catalytic Performance of SCNPs-Pt(0)**

In order to confirm the final valence state and additional content of platinum in the nanoparticles, XPS of SCNPs-Pt(0) was measured (shown in Fig. 4d). The doublet peaks appearing at 71.0 and 74.3 eV are typical characteristics of zero valence platinum. This proves that the divalent platinum ions in SCNPs are successfully reduced to zero valence state by NaBH$_4$, and the content of platinum is below 7 wt% in SCNPs-Pt(0).

In order to verify the catalytic effect of SCNPs-Pt(0), a classical platinum-catalyzed reduction of 4-nitrophenol by sodium borohydride can be carried out in a mixed solvent. 4-Nitrophenol and sodium borohydride were added to the mixed solvent with pH 10. After the catalyst was added, the ultraviolet-visible spectroscopy was employed to demonstrate the catalytic properties of SCNPs-Pt(0) as shown in Fig. 5. It can be clearly seen that the absorbance of the band at 400 nm decreases with increasing time, which is the result of the continuous reduction of 4-nitrophenol. There appears a new band at 310 nm, which is the absorption caused by the product $p$-aminophenol in the reduction process. Of course, the absorbance of this peak increases with increasing time. Under the same condition, it can be seen that the catalytic performance of platinum in SCNPs (Figs. 5a and 5b) is much better than that of uncross-linked polymer carried Pt(0) particles (Fig. 5c). Pt(0) atoms dispersed in SCNPs-Pt(0) are partially stabilized by coordinating groups and partially trapped by the reticular structure in SCNPs. The most interest-

### Table 1  Comparison of GPC and DLS data for P(St-co-PPh-co-BCB), P(St-co-PPh-co-BCB)-Pt(II), and SCNPs-Pt(II).

| BCB (mol%) | $M_n$ | PDI | $D_h$ (nm) | $M_n$ | PDI | $D_h$ (nm) | $M_n$ | PDI | $D_h$ (nm) |
|-----------|-------|-----|-----------|-------|-----|-----------|-------|-----|-----------|
| 20        | 15100 | 1.88| 24        | 8700  | 1.96| 20        | 6000  | 1.97| 14        |
| 10        | 12600 | 1.72| 21        | 8600  | 1.85| 19        | 6400  | 1.78| 16        |
| 5         | 13500 | 1.69| 21        | 8800  | 1.82| 19        | 7600  | 1.79| 17        |

a Molar content of BCB units was calculated by feed ratio. b Hydrodynamic diameter ($D_h$) was measured by DLS in tetrahydrofuran; the concentration of the samples was 0.5 mg mL$^{-1}$. c Apparent $M_n$ of P(St-co-PPh-co-BCB)-Pt(II) and SCNPs-Pt(II) was measured by GPC.

**Fig. 4** TEM images of (a) taper P(St-co-PPh-co-BCB)-Pt(II) and (b) quasi-circular SCNPs-Pt(0) (the content of BCB is 20%), the diameter is 3−10 nm; (c) Particle size distribution of SCNPs-Pt(0) (the content of BCB is 20%); (d) XPS result of SCNPs-Pt(0).
ing thing is that too higher or too lower content of cross-linker in SCNPs cannot get the best catalytic properties, as shown in Fig. 5(d). That is to say, to adjust the density and morphology of the reticular structure in SCNPs is one of the key factors to control the state and size of Pt(0) in SCNPs. Another possible factor is the type and density of the coordinat-

ing groups in SCNPs.

CONCLUSIONS

Herein, a fabricating approach for platinum atoms dispersed in single-chain nanoparticles is proposed. After the collapse and intramolecular cross-linking of single polymer chains, SCNPs have the reticular structure with suitable coordinating groups, which are suitable for the separation and stabilization of metal atoms. The confined interspace can prevent metal atoms from assembling with each other, and the discrete chain allows the solution to contact the catalyst. Pt(0) steadily and atomically dispersed in SCNPs exhibit better catalytic properties for the reduction of p-nitrophenol to p-aminophenol than normal polymer carried platinum particles. However, to characterize the detailed state and morphology of these metal atoms in SCNPs is still a challenge at this stage. Further research on the percentage of single platinum atoms in SCNPs as well as the relation between this percentage and the inner space and structure of SCNPs will be interesting in future work. It will be not only a breakthrough to develope the precious metal catalysts with miraculous properties, but also a direction for the application of SCNPs.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-021-2499-x.

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