Polymer 64 (2015) 216–220

Contents lists available at ScienceDirect

Polymer

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

Synthesis of soluble conjugated polymeric nanoparticles through heterogeneous Suzuki coupling reaction

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ARTICLE INFO

Article history:
Received 8 December 2014
Received in revised form
29 January 2015
Accepted 3 February 2015
Available online 11 February 2015

Keywords:
Heterogeneous catalysis
Suzuki polycondensation
Hyperbranched polymers

ABSTRACT

Conjugated hyperbranched polyphenylene nanoparticles are fabricated by cross coupling reactions between an A_2 type monomer 1,4-phenylenediboronic acid (**1**) and B_3 type monomers 1,3,5-triiodobenzene (**2**) and 1,3,5-tribromobenzene (**3**). The Suzuki-type polycondensation was conducted with a highly efficient heterogeneous catalyst to give conjugated polymeric nanoparticles which are soluble in a variety of organic solvents. The growth of the hyperbranched polyphenylenes are controlled and eventually terminated by the decomposition of the boronate terminal groups in basic aqueous media in the heterogeneous catalysis system. This method represents a new approach to produce soluble conjugated polymeric nanoparticles with simple and symmetrical monomers with more than two end groups ($A_x + B_y$, $x \geq 2$, $y > 2$).

1. Introduction

Conjugated microporous polymers (CMPs) are a new class of porous materials which enable the elaborate integration of porosity, conjugation, and synthetic diversity and have been gradually utilized in gas adsorption [1–3], electrical energy storage [4], heterogeneous catalysis [5], and chemical sensors [6,7]. However, most of these polymers are insoluble in organic solvent, leaving difficulties in processing and property characterizing, and limiting further applications of the CMPs in some novel fields like organic light emitting diodes (OLEDs) [8,9], organic solar cells [10,11] and light-harvesting antenna [12]. The latest work towards the solubilization of CMPs mainly involves reprecipitation methods [13–18] and emulsion techniques [19,20], resulting in solution-dispersible nanoparticles with a large particle size. The first truly soluble CMPs (SCMPs) came to Cooper's work [21], where the molecular weights and sizes of SCMPs were mediated by introducing a disubstituted pyrene monomer. Soluble dendritic pyrenes were also fabricated via a generation-by-generation technique (GBGT) [22]. While this GBGT showed more advantages in controlling the size of SCMPs, tedious synthetic procedures were typically required. Bo et al. reported a new family of fluorescent hyperbranched polymers through an "AB_2 + AB" approach. The SCMPs obtained were further used in blue light emitting materials [23]. Recently, we reported a size-controlled synthesis of SCMPs in homogeneous system with $A_x + B_y$ ($x \geq 2$, $y > 2$) monomers [24]. The sizes of the SCMP nanoparticles were regulated by tuning the pore sizes of the nanoreactors where the confined growth of the SCMPs took place.

Herein, we report the synthesis of SCMPs through heterogeneous Suzuki polycondensation between an A_2 monomer (1,4-phenylenediboronic acid) and B_3 monomers (1,3,5-triiodobenzene or 1,3,5-tribromobenzene) catalyzed by palladium nanoparticles embedded on the surface of silica-supported carbon nanomembranes (Pd@SBA-15©) [25,26]. The decomposition of arylboronic acid [27] when heated for a prolong time in aqueous solution are widely recognized as a great challenge (side reactions) in the fabrication of polymers through Suzuki coupling reaction due to the termination effort. However, this slow (side) reaction played a vital role in the size-controlled synthesis of SCMPs in this work. Based on this strategy, we adopted the heterogeneous polycondensation system where tetrabutylammonium bromide (TBAB) acted as a porter to carry A_2 monomer toward Pd@SBA-15© catalyst, and the decomposition of arylboronic acid simultaneously regulated the growth of nanoparticles, successfully obtaining the SCMPs with strong photoluminescence. The sizes of the SCMPs were

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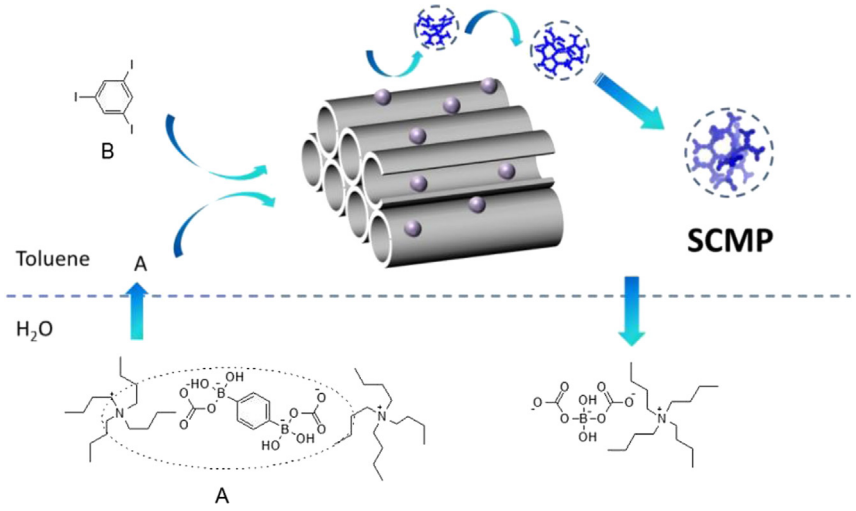
http://dx.doi.org/10.1016/j.polymer.2015.02.006
0032-3861/



Scheme 1. Schematic illustration of the synthesis of SCMPs through heterogeneous Suzuki polycondensation.

measured as sub-10 nm with narrow size distributions which had been considered as a prospective target in the applications of these SCMPs [15].

2. Experimental sections

Materials: All chemical reagents were commercial grade and used as received unless otherwise stated. 1,3,5-Tribromobenzene, 4-methoxyphenylboronic acid and 4-iodotoluene were purchased from Aladdin (China). 1,4-Phenylenediboronic acid was purchased from Energy Chemical (China). 1,3,5-Triiodobenzene [28] was prepared according to reported methods with minor modification. The Pd@SBA-15© catalyst was prepared according to our recently published procedure [29].

Characterizations: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker AVANCE 400 FT-NMR spectrometer in $CDCl_3$. The hydrodynamic diameters of the SCMPs in DMF were analyzed using a Zetasizer Nano at 25 °C (Malvern, UK) and reported as the number average diameters. The fluorescence emission spectra of the SCMPs in THF were obtained on a Fluorolog-3-P UV-VIS-NIR fluorescence spectrophotometer (Jobin Yvon, France) and UV-vis spectra were collected using a UNICO UV-21-2 PCS spectrometer. The palladium contents of the samples were analyzed by ICP-AES on a Thermo Elemental IRIS 1000 instrument.

2.1. Synthesis of soluble conjugated microporous polymers (SCMPs)

2.1.1. Polycondensation

a. 1,3,5-Triiodobenzene (0.228 g, 0.5 mmol), 1,4-phenylenediboronic acid (0.149 g, 0.9 mmol), TBAB (0.081 g, 0.25 mmol), Pd@SBA-15© (10 mg) were successively added to a 25 mL sealed tube. And then 2 M K_2CO_3 solution (1 mL) was poured into the sealed tube in N_2 atmosphere, followed by a quickly degassing step for three times, and then toluene (1 mL) was added into the system at a freeze condition. After degassed by three freeze–pump–thaw cycles, the tube was sealed and the mixture was stirred at 80 °C for 120 h (entry 3).

b. 1,3,5-Tribromobenzene (0.157 g, 0.5 mmol), 1,4-phenylenediboronic acid (0.373 g, 2.25 mmol), TBAB (0.081 g, 0.25 mmol), Pd@SBA-15© (10 mg) were successively added to a 25 mL sealed tube. And then 2 M K_2CO_3 solution (1 mL) was poured into the sealed tube in N_2 atmosphere, followed by a quickly degassing step for three times, and then xylene (1 mL) and ethyl alcohol (0.5 mL) was added into the mixture at a freeze condition. After degassed by three freeze–pump–thaw cycles, the tube was sealed and the mixture was stirred at 120 °C for 120 h (entry 11).

2.1.2. Purification

After polycondensation, the resulting mixture was cooled to room temperature and neutralized with 2 M hydrochloric acid (1 mL), and then the mixture was adsorbed on silica gel (4 g). The powder was washed with adequate amount of water to remove TBAB and then Soxhlet extracted with THF for 24 h. After removal of THF by rotary evaporation, the polymer was purified by precipitation in methanol to give the desired product as white solid after dried under vacuum for 12 h at 70 °C.

3. Results and discussion

Scheme 1 illustrates the synthesis of SCMPs through heterogeneous polycondensation. The diboronic acid monomer (A_2) is

Table 1
The effect of solvents and TBAB on the SCMPs.

Entry	Monomer	Solvent	TBAB/PhX_3[e]	M_n[f]	PDI[f]	Yield%
1	1[a,b]	Toluene/H_2O (1:1)	0:1	1098	1.66	5
2	1[a,b]	Toluene/H_2O (1:1)	0.25:1	1823	1.83	62
3	1[a,b]	Toluene/H_2O (1:1)	0.5:1	1396	1.78	53
4	1[a,b]	Toluene/H_2O (1:1)	1:1	1350	2.11	47
5	1[a,b]	Toluene/H_2O (1:1)	2:1	678	1.75	10
6	1[a,b]	Toluene/H_2O (1:1)	10:1	890	1.26	4
7	1[a,c]	Toluene/H_2O (1:1)	0.5:1	2180	1.85	82
8	1[a,b]	Toluene/EtOH/H_2O (1:0.5:1)	0.5:1	/	/	[g]
9	2[d,c]	Xylene/H_2O (1:1)	0.5:1	1107	1.35	14
10	2[d,c]	Xylene/EtOH/H_2O (1:0.5:1)	0.5:1	1277	1.40	54
11	2[d,c]	Xylene/EtOH/H_2O (0.5:0.25:1)	0.5:1	1308	1.37	63

[a] Reaction temperature, 80 °C.
[b] Molar ratio of functional groups between 1,4-phenylenediboronic acid and PhX_3 is 1.2:1.
[c] Molar ratio of functional groups between PhX_3 and 1,4-phenylenediboronic acid is 3:1.
[d] Reaction temperature: 120 °C.
[e] Molar ratio of TBAB and PhX_3.
[f] Apparent molecular weights and molecular weight distributions were measured using GPC with PS calibration.
[g] Crosslinked.