Applied Surface Science 419 (2017) 744–752

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Synthesis and characterization of hydrophobic amino-based polyphosphazene microspheres with different morphologies via two strategies

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ARTICLE INFO

Article history:
Received 3 March 2017
Received in revised form 14 April 2017
Accepted 28 April 2017
Available online 1 May 2017

Keywords:
Polyphosphazene
Amino-based microspheres
Fluorinated
Precipitation polymerization
Hydrophobicity

ABSTRACT

Novel fluorinated cross-linked polyphosphazene microspheres bearing active amino groups on the surface have been successfully prepared by precipitation polymerization of hexachlorocyclotriphosphazene (HCCP) with 2,2′-bis(trifluoromethyl)-4,4′-diaminodiphenyl ether (6FODA) through different strategies: ultrasonic in high temperature and water-triggered self-assembly in normal temperature. By adjusting the reaction conditions, the diameter of the microspheres were controlled from 0.5–3 μm and 0.2–1 μm respectively. The chemical structures, morphologies, thermal properties, and surface properties of these microspheres were investigated by Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA), and water contact angles (WCA). The cross-linked structures exhibited remarkable thermal stability, and no glass transition temperatures were observed. It was found that a wafer coated with those prepared microspheres has a water contact angle around 135°, which definitely increased compared with the water contact angle of as-prepared poly(hexachlorocyclotriphosphazene-co-4,4′-diaminodiphenyl ether) microspheres (about 8.8°).

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1. Introduction

Polyphosphazene-based polymers are organic-inorganic hybrid macromolecules consist of over 700 members, they have attracted much attention in many scientific fields due to their wide potential application because of the unique structure [1]: a main chain (-P=N-) with two of the same or different organic side groups attached to each phosphorus atom [2]. It has been showed in previous studies that the postpolymerization modification on polyphosphazenes have a significant influence on their properties [3–6]. Accordingly, the substituted derivatives of polyphosphazenes can be applied in plenty of different aeras, such as elastomers [7], biomedical materials [8,9], flame-resistant [10], electronic materials [11] or ceramics [12], to mention just a few. However, preparation of the linear polyphosphazenes is not plain, the conventional ring opening polymerization route from hexachlorocyclotriphosphazene(HCCP) requires harsh synthesis conditions(250 °C in vacuum), and the obtained polymer shows a wide molecular weight distribution (PDIs–10) [13]. Despite intensive efforts in pioneering researches, mass-produce of the linear polyphosphazenes has not been realized.

Another kind of phosphazene-containing material, which attracted attention during the last decade is cyclomatrix-type polyphosphazenes. Here, the phosphazene rings are linked by exocyclic groups to form crosslinked matrices. This new type of polyphosphazene, which was developed by Tang's group, can be prepared by precipitation polycondensation based on nucleophilic substitution using HCCP and aromatic organic monomers bearing dual-nucleophilic groups [14]. Since this strategy been developed, several aromatic monomers, such as 4,4′-sulfonyldiphenol [15], benzidine [16], phloroglucinol [17], and 4,5-dibromofluorescein [18] have been used to fabricate cyclomatrix-type polyphosphazenes, to form micro- and nanosized materials, mainly including nanotubes [19], nanofibers [20] and microspheres [21].

The polymeric microspheres have been paid extensive attention in many fields of scientific research owing to their distinctive properties compared with plentiful materials. Because of the diverse functionality and tunable surface characteristic, microspheres may

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http://dx.doi.org/10.1016/j.apsusc.2017.04.236
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find promising applications in chromatograph separation [22], energy storage [23], sensors [24], coatings [25], drug delivery [26], and in other areas. In particular, the microspheres with amino groups, due to their intriguing liveness and the instinct of attaching a variety of proteins and other biologically active molecules, are specially interested [27,28]. So far, there are two major methods to fabricate microspheres linking amino groups: dispersion polymerization and blending. Nevertheless, these traditional methods all need multiple steps or contain the utilization of stabilizing agents [29–31]. The strategy of fabricating cyclomatrixpolyphosphazenes has made a great progress to deal with this difficulty. Zhang et al. successfully synthesized high cross-linked microspheres bearing active amino groups on the surface via a single-step precipitation polymerization of HCCP with 4,4′-diaminodiphenyl ether (ODA) in acetonitrile medium without any added surfactant [32]. Up till now, a few typical kinds of polyphosphazene microspheres with amino groups have been fabricated [33,34]. Despite many possibilities for functionalization and application of these crosslinked microspheres, the number of publications over the past several years in this field is limited. Generally, these microsphere materials are hydrophilic own to the hydrophilicity of the amino groups. Therefore, developing the hydrophobicity of amino-based polyphosphazene microspheres may offer new opportunity for their further applications.

To date, almost all of the synthesis of cross-linked amino-based polyphosphazene microspheres has been carried out by means of precipitation polymerization under high-temperature ultrasonic conditions. Such conditions can facilitate the process of polymerization and promote the dispersion of colloids during the reaction. Yet, they also increase the complexity of the reaction and make it difficult to control. Simultaneously, when the need to expand the scale of the reaction, the heating will consume more energy, and high-power ultrasound will cause harm to human health. In the study reported herein, we prepared 2,2′-bis(trifluoromethyl)-4,4′-diaminodiphenyl ether (6FODA) as monomers. Then, presenting a novel covalently cross-linked poly(HCCP-co-6FODA) microspheres (CP-6FODA) with activity amino groups by HCCP and 6FODA via two methods: a single-step precipitation polymerization by ultrasonic in high temperature and a water-triggered self-assembly precipitation polymerization by stirring in normal temperature. The hydrophobic surface with low surface energy hydrophobic groups (-CF3) was then produced by dripping the microspheres solution onto the substrate followed by fast evaporation of the solvent. Then, water contact angle (WCA) measurements were occupied to explore the influence of the trifluoromethyl groups on CP-6FODA in comparison to previously prepared poly(hexachlorocyclotriphosphazene-co-4,4′-diaminodiphenyl ether) microspheres (CP-ODA) and poly(hexachlorocyclotriphosphazene-co-2-trifluoromethyl-4,4′-dinitryldiphenyl ether) microspheres (CP-3FODA).

2. Experimental

2.1. Materials

HCCP was purchased from Shandong Lanyin Chemical Co. Ltd., China and recrystallized from petroleum ether followed by sublimation (60 °C and 0.05 mmHg). 4-Nitro-2-(trifluoromethyl)phenol, 1-chloro-4-nitro-2-(trifluoromethyl)benzene, K_2CO_3, Fe, NH_4Cl, and acetyl chloride were purchased from commercial sources and used without further purification. Triethylamine (TEA) was distilled over calcium hydride. All solvents were purchased from commercial sources and purified with standard methods.

2.2. Synthesis of 2,2′-bis(trifluoromethyl)-4,4′-dinitryldiphenyl ether

All processes were conducted in a dry nitrogen atmosphere. In a 100 mL flask, 4-nitro-2-(trifluoromethyl)phenol (10.36 g, 0.05 mol) and 1-chloro-4-nitro-2-(trifluoromethyl)benzene (11.28 g, 0.05 mol) were dissolved in 50 mL N,N-dimethylformamide(DMF), after adequately stirred, K_2CO_3 (6.91 g, 0.05 mol) was added to the mixture and stirred at room temperature for 30 min. The reaction was then stirred at 120 °C for 12 h. After it was cooled to room temperature, the mixture was poured into cold water and adjusted to a pH value of 7 with diluted hydrochloric acid giving a yellow precipitate. After filtration, the crude product was washed with distilled water twice and then recrystallization with methanol/DMF to obtain purified product as a faint yellow solid in 82.6% yield (16.36 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.35 (d, 2H), 8.27 (d, 2H), 8.46 (d, 2H).

2.3. Synthesis of 2,2′-bis(trifluoromethyl)-4,4′-diaminodiphenyl ether (6FODA)

Fe powder (6.72 g, 0.12 mol, 3 equiv) and NH_4Cl (6.42 g, 0.12 mol, 3 equiv) were added sequentially to a solution of 2,2′-bis(trifluoromethyl)-4,4′-dinitryldiphenyl ether (15.84 g, 0.04 mol, 1 equiv) in EtOH/H_2O (3:1) and then refluxed at 90 °C overnight under nitrogen atmosphere. A black suspension was obtained. After filtration, the clarified liquid was poured into cold water giving a white solid. The crude product was obtained by filtration and then washed with distilled water twice. We provided the crude product by recrystallization with EtOH to afford 6FODA as a yellowish powder with a yield of 65.2% (8.76 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.87 (s, 4H), 6.65 (d, 2H), 6.84 (d, 2H), 7.10 (s, 2H). The synthetic route for the preparation of 6FODA is depicted in Scheme 1.

2.4. Synthesis of CP-6FODA microspheres through ultrasonic method

In a typical procedure, 2 mL of triethylamine (TEA) was added to a round-bottomed flask containing 0.1 g (0.29 mmol) of HCCP, 0.29 g (0.87 mmol) of 6FODA and 50 mL of acetonitrile. The polycondensation was conducted in an ultrasonic bath (150W, 40 kHz) at 60 °C for 8 h. After reaction, the precipitated product was isolated by centrifugation, washed three times using ethanol and deionized water, respectively, and then dried in vacuum at 50 °C to yield CP-6FODA as a yellowish powder. We also synthesized CP-6FODA using different concentrations of monomers (HCCP concentrations: 1, 2, 4, and 6 mg mL^{-1}). The molar ratio of 6FODA to HCCP was 3:1.

2.5. Synthesis of CP-6FODA microspheres through water-triggered self-assembly polycondensation method

All processes were proceeded under the protection of dry nitrogen. In a typical procedure, 0.1 g (0.29 mmol) of HCCP and 0.29 g (0.87 mmol) of 6FODA was added to a round-bottomed flask, dissolved in 50 mL of acetonitrile. After fully stirred in room temperature for 15 min, 2 mL of triethylamine (TEA) was added dropwise. Then, the system was maintained stirring for 24 h to yield CP-6FODA oligomer solution.

60 mL of deionized water was added dropwise into the oligomer solution over 20 min under stirring conditions. Then, keep stirring for 30 min. After reaction, the precipitated product was isolated by centrifugation, washed three times using ethanol and deionized water, respectively, and then dried in vacuum at 50 °C to yield CP-6FODA as a yellowish powder. The products were also synthesized using different concentrations of monomers same as the ultrasonic method.

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