

# Preparation of hierarchical polyimide hollow spheres via a gas bubble templated transimidization induced crystallization process

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**Abstract** Hierarchical polyimide hollow spheres consisting of crystalline nanoparticles were synthesized by a novel gas bubble templated transimidization induced crystallization process. The morphologies of the hollow spheres can be fine-tuned by changing the concentrations and the chemical structure of the monomers. Based on the experimental results, a possible formation mechanism of these polyimide hollow spheres was proposed based on the aggregation of the primary crystalline polyimide nanoparticles on the in situ formed gas bubbles as soft templates to minimize the interfacial energy.

**Keywords** Polyimides · Bubble template · Hollow spheres · Transimidization induced crystallization

## Introduction

The fabrication of hollow spheres with controllable morphologies has attracted great attention in recent decades, due to their widespread applications as catalysts, low-dielectric fillers, adsorbents, and drug delivery carriers. Many hollow spheres consisting of metals, ceramics, or polymers have been synthesized so far, the preparation methods can be generally divided into two categories based on the properties of templates: soft templates (micelles, block copolymer aggregates, etc.) and hard templates (silica, polymer nanoparticles, etc.) [1–5]. For hollow spheres, mechanical strength and thermal stability are often required, polyimides are a class of representative high performance polymers with high thermal stability and good mechanical properties [6], thus a facile and reproducible preparation of PI hollow

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spheres will clearly benefit many applications. However, mainly due to the intractability of most aromatic PIs, there are only a few reports on the preparation of porous PI micro/nanoparticles [7–10]. Oikawa reported the preparation of porous PI nanoparticles using a second polymer (poly(acrylic acid), etc.) as porogen [11, 12]. He further fabricated PI spherical nanoparticles with intriguing shapes, like doughnut-like and soccer ball-shaped morphologies, unfortunately, the reproducibility of that experimental procedure was poor, and the hollow spheres were rarely obtained [13]. Very recently, we provided a facile and reproducible reprecipitation method for the fabrication of PI hollow spheres [14], through fine-tuning the polymer precursor concentration or adding extra inorganic salt, many uniquely shaped objects, including hollow spheres, deflated capsules, bowl-shaped particles, and dimple-like hollow spheres can be obtained. However, all the above-mentioned polyimide hollow spheres are amorphous, while the crystallinity of PIs provides advantages, such as high solvent resistance and dimensional stability at higher temperature, these features make the study of the crystalline behavior and morphological features of PIs particularly attractive. Recently, Kimura developed reaction-induced crystallization as a powerful strategy for the morphology control of aromatic polymers to overcome the antagonistic problem between intractability and morphosynthesis [15, 16], the principle of this approach is that when the degree of polymerization of the oligomers exceeds a critical value, they will precipitate from the solution to form nuclei, the nuclei gradually growth into crystals with various morphologies. Crystalline PIs with complex micro/nanostructures, such as microspheres, microflowers, and nanofibres have been synthesized [17–19]. However, less attention has been paid to the preparation of crystalline PI hollow spheres.

The transimidization reaction as a method for the preparation of PIs has been known for decades, it was originally proposed by G.E. Plastics in the synthesis of ultrahigh pure dianhydrides by blocking the anhydride with an electron-deficient amine (such as aminopyridine and aminopyrimidine), a transimidization reaction would readily take place between the blocked dianhydride and electron-rich aryl amine (such as aniline) [20, 21]. However, except for a few cases, this transimidization reaction has been largely ignored [22, 23]. In this communication, we reported the preparation of hierarchical polyimide hollow spheres for the first time through a transimidization induced crystallization process, PI hollow spheres consisting of crystalline nanoparticles were readily obtained. Besides, a possible formation mechanism was also proposed based on the aggregation of primary crystalline PI nanoparticles on the in situ formed gas bubble template.

## Experimental section

### Materials

Pyromellitic dianhydride (PMDA) and 3,3',4,4'-tetracarboxybiphenyl dianhydride (BPDA) were purchased from Shanghai institute of synthetic resins and used after drying at 150 °C for 5 h in vacuum. 3,5-Diamino-1,2,4-triazole (DAT),

*p*-Phenylenediamine (PPDA), 2-aminopyridine (AP), and 2-aminopyrimidine (AM) were purchased from Sigma-Aldrich and used as received. DBT solvent (a mixture of structural isomers of dibenzyltoluene) was purchased from Yingkeli Co. Ltd., *m*-cresol was used after distillation over P<sub>2</sub>O<sub>5</sub>.

### Synthesis of 2-aminopyridine blocked dianhydride PMDA-AP

Pyromellitic dianhydride (PMDA) (1.000 g, 4.58 mmol), 2-aminopyridine (AP) (0.9493 g, 10.09 mmol), and *m*-cresol (40 ml) were placed in a three-necked flask fitted with a nitrogen inlet, after stirring for 15 min under nitrogen flow, isoquinoline (5 drops) was added, and the solution was heated to reflux overnight under a nitrogen atmosphere. After that, the homogeneous solution was cooled and poured into large amount of methanol (400 mL), the light-green precipitates were collected, washed several times with ethanol and then dried in vacuum (40 °C) for 24 h; 1.20 g (62% yield).

### Preparation of PI hollow spheres through transimidization induced crystallization

10 mL of DBT was placed into a cylindrical flask, after stirring for 15 min in a nitrogen flow, it was heated to 350 °C, the diamine DAT (1 mmol) was added to the solution and dissolved immediately. Another solution of blocked dianhydride PMDA-AP (1 mmol) in 10 mL of DBT was also heated to 350 °C, it was then added to the DAT solution at 350 °C under stirring (or vice versa: the DAT solution was added to the PMDA-AP solution). The stirring was continued for about 10 s, and then the polymerization was carried for 8 h without stirring. After that, the precipitates were obtained by centrifugation, washed several times with ethyl acetate, and then dried at 80 °C for 6 h.

### Measurements

The chemical structures were characterized by Infrared (IR) spectra with a Nicolet 560 spectrometer. The morphology of the polyimides was observed by SEM (Inspect F scanning electron microscope at 20 kV) and TEM (JEM 100CX II transmission electron microscopy at 80 kV). WAXS powder patterns were recorded on an X'Pert Pro MPD diffractometer at 30 kV and 15 mA with a scanning rate of 1° min<sup>-1</sup>. The degree of crystallinity was calculated based on the areas of crystalline peaks and amorphous halo by the software of X'Pert Pro MPD diffractometer.

## Results and discussion

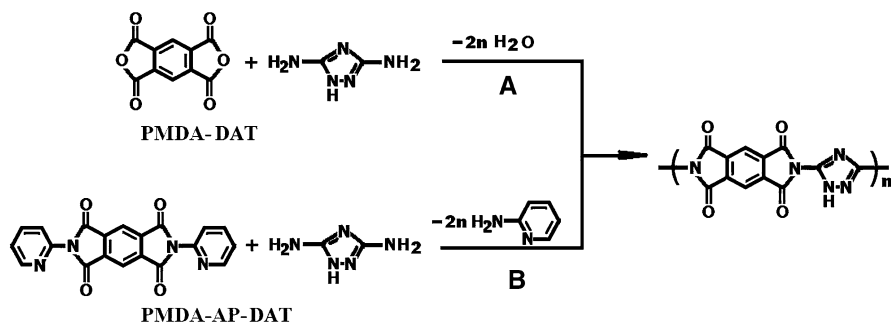
Two approaches for the morphological control of PIs were carried out as shown in Scheme 1, one is a direct imidation induced crystallization process (PMDA-DAT) between dianhydride and diamine with the elimination of water, and the other is a

novel transimidation induced crystallization process between blocked dianhydride and diamine (PMDA-AP-DAT) with the elimination of 2-aminopyridine.

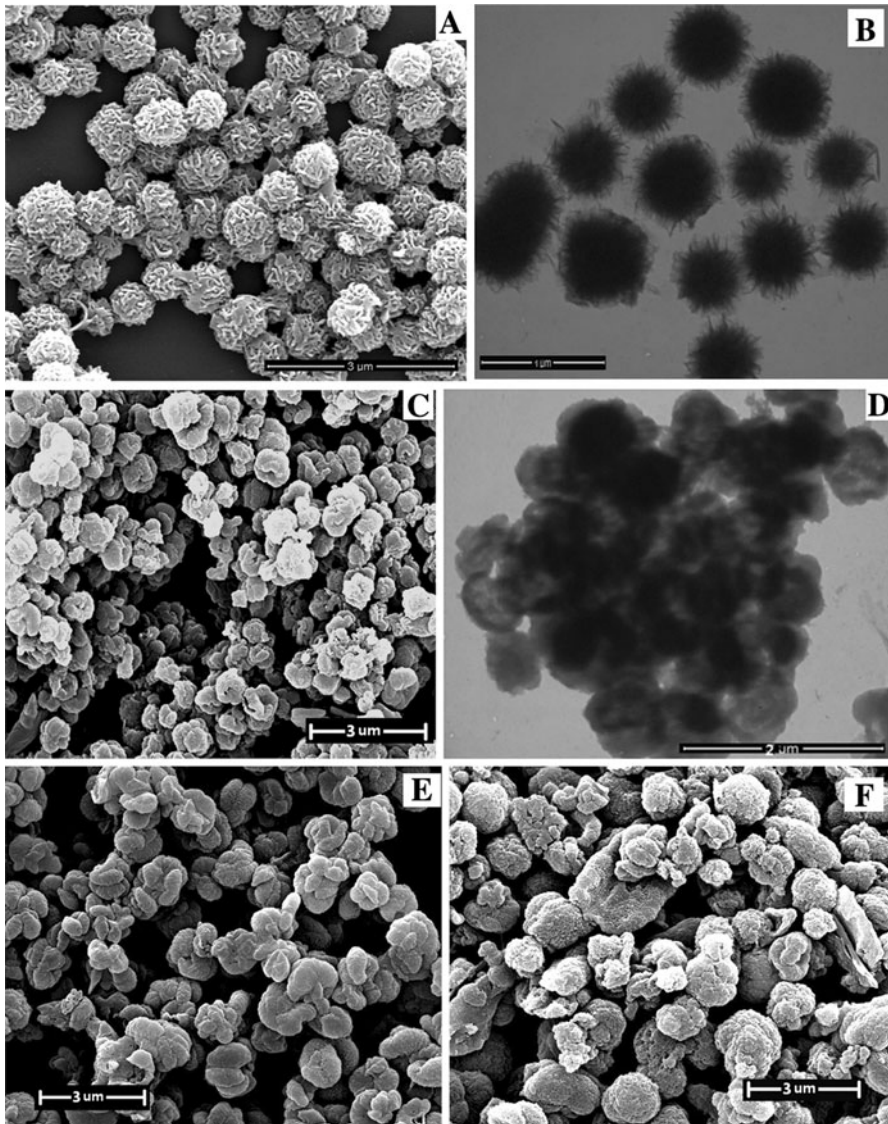
The processes were carried out at 350 °C in DBT solution at a concentration of 0.5–1.5%. The solutions became turbid immediately due to the reaction-induced crystallization and precipitation of PI nanoparticles, the resulted products were collected by filtration, and the morphologies of the formed PIs were characterized by SEM and TEM (Fig. 1).

As shown in Fig. 1, the direct imidation process at a concentration of 1% yielded microspheres with sub-micrometers, the spheres were composed of nanoplates with thickness about 50 nm (Fig. 1a). When the polymerization was carried out by the transimidation process, the morphology of the resulted PIs is drastically changed; at the same concentration of 1%, large number of irregular spherical aggregates with sub-micrometer were formed, the microspheres were composed of nanoparticles with diameter about 50 nm (Fig. 1c), some of the spheres were broken, and hollow interior can be clearly identified. The morphological change from microspheres to hollow spheres can be further confirmed by the corresponding TEM images, the PIs prepared by direct process were microsphere with dark center and gray edge, revealed they were solid spheres composed of nanoplates (Fig. 1b). On the contrary, the PIs prepared by transimidation process were microspheres with gray center and dark circle, revealed their hollow sphere structures (Fig. 1d). When the concentration of the solution was further increased to 1.5%, irregular hollow sphere with diameter about 1  $\mu\text{m}$  were also formed (Fig. 1e). The monomer adding sequence on the resulted polyimide morphology was also investigated by reversal the order of monomer adding sequence, that means the DAT solution was added to the PMDA-AP solution, polyimide hollow spheres with diameter about 1  $\mu\text{m}$  were also observed (Fig. 1f).

In order to shed some light on the growing process of PI hollow spheres, we quenched the transimidation induced crystallization process at different stages. The transimidation process was stopped immediately when the solution turned turbid, SEM revealed large number of hollow spheres with broken shell (Fig. 2a), this maybe due to that at the initial stage of transimidation process, the solid content of PI primary nanoparticles is too low to form a continuous shell, thus PI



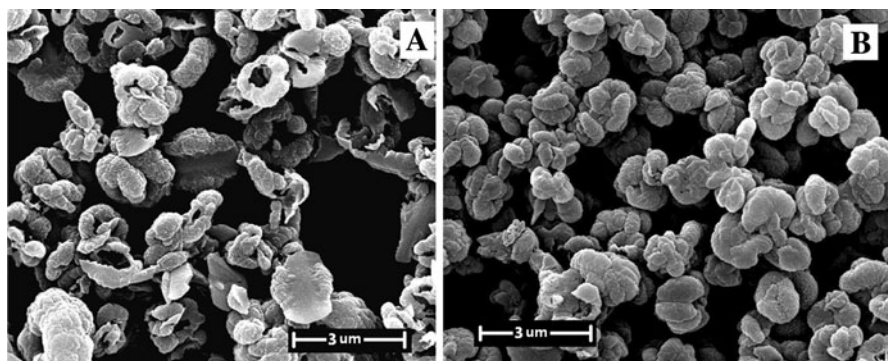
**Scheme 1** Synthesis of polyimide with controllable morphologies via A: direct imidization induced crystallization (PMDA-DAT) and B: transimidation induced crystallization (PMDA-AP-DAT)



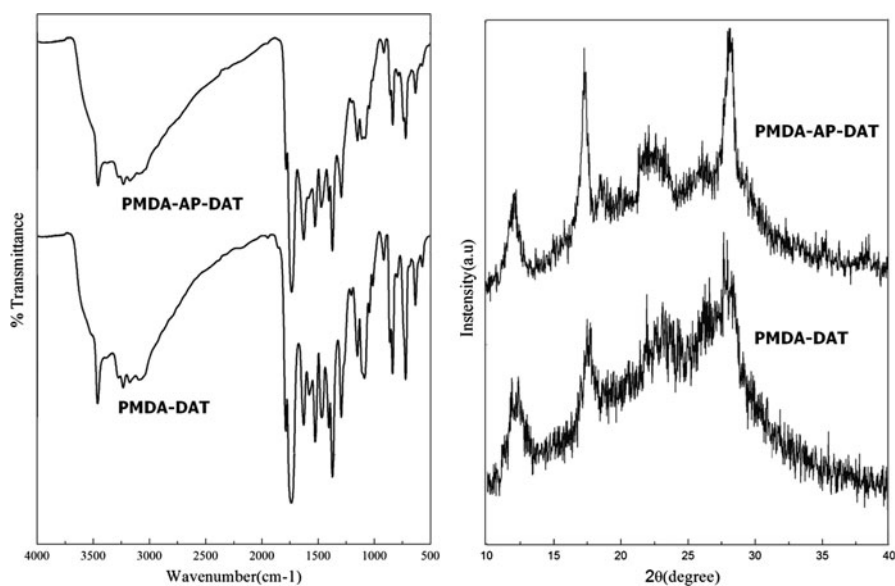
**Fig. 1** SEM (a) and TEM (b) images of polyimides prepared by direct imidization process (PMDA-DAT) at a concentration of 1%; SEM (c) and TEM (d) images of PIs prepared by transimidization process (PMDA-AP-DAT) at concentration 1%; SEM image of PIs prepared by transimidization process at a concentration of 1.5% (e) and vice versa process at a concentration of 1.5% (f)

hollow spheres with open holes were formed. With the reaction process prolonged, the PI nanoparticles gradually increased and gradually formed hollow spheres with complete shell (Fig. 2b).

The obtained polyimide hollow spheres were insoluble in any organic solvents, and therefore their chemical structure was mainly analyzed by FT-IR spectroscopy



**Fig. 2** SEM images of PIs prepared by transimidization process (PMDA-AP-DAT): **a** just after the solution turns turbid, and **b** after 3 h at a concentration of 1.5%



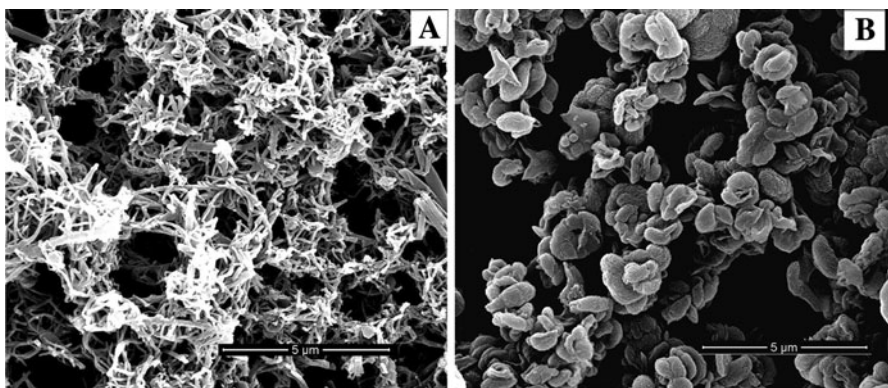
**Fig. 3** FTIR absorption spectrum (*left*) and WAXD pattern (*right*) of polyimides prepared by direct imidization process (PMDA-DAT) (*lower*) and transimidization process (*upper*) at a concentration of 1%

(Fig. 3a). The PI prepared by transimidization process showed bands of C=O stretching of the imide group clearly at  $1,785$  and  $1,736\text{ cm}^{-1}$ , and band of C=N stretching that attributed to the deformation of the imide ring or the imide carbonyl groups at  $1,373$  and  $720\text{ cm}^{-1}$ , respectively. This spectrum is very similar to polyimide prepared by direct imidization process. Bands characterized as that of anhydride group ( $1,854\text{ cm}^{-1}$ ) were not observed, this result showed that high molecular weight PIs were prepared [24]. X-ray diffraction further revealed the crystalline nature of the PI hollow spheres (Fig. 3b), although a broad amorphous halo was detected, sharp reflections corresponding to crystals were also clearly

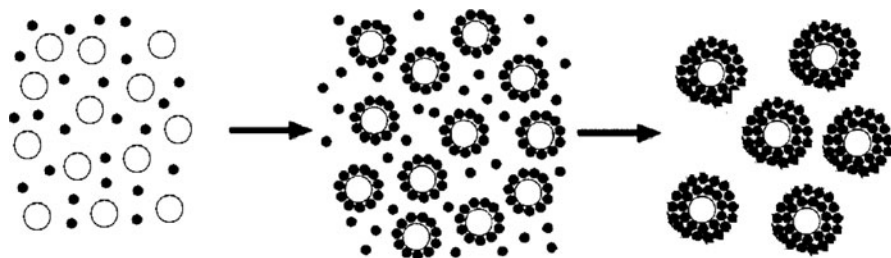
observed, in contrast. Even though there are several reports on the preparation of porous polyimide spheres, those composed of crystalline polyimides have been rarely revealed, and most commercial polyimide films and molds are also amorphous. A detail calculation resulted that the degree of crystallinity of the PI prepared by transimidization process is about 10% higher than that prepared by direct imidization process, which means besides the interesting hollow sphere structure, the transimidization process still holds the benefit of enhancing the crystallinity of the resulted polyimides.

Even though hollow spheres are clearly more effective for many applications, there are only a few reports on the preparation of PI hollow spheres due to the intractability of aromatic PI, so we further explore whether this transimidization induced crystallization process can be extend to the preparation of PI hollow spheres with different chemical structures. The dianhydride monomer PMDA was replaced by BPDA, direct reaction between BPDA and DAT resulted in a mixture of nanofibers and nanobelts (Fig. 4a). However, when the transimidization process was taken, hollow sphere with diameter about 1.5  $\mu\text{m}$  were obtained, which confirmed the universality of this novel method. But when the diamine DAT was replaced by other monomer such as PPDA, no hollow sphere morphology can be observed, which means the transimidization induced crystallization as a novel method for the preparation of PI hollow spheres can only be valid in a limited extension.

A good understanding of the formation mechanism behind such a novel process for preparing hierarchical PI hollow spheres with crystalline structure is of great interest. Based on the above experimental results and some controlled experiments, we propose a gas bubble templated mechanism to illustrate the formation of hierarchical PI hollow spheres (as shown in Scheme 2). Gas bubbles dispersed in a liquid host have recently emerged as promising soft templates for the synthesis of hollow spheres [25]. For example, ZnSe hollow spheres were synthesized under hydrothermal conditions using  $\text{N}_2$  gas bubbles as soft templates [26]. ZnS hollow nanospheres were prepared via aggregation of small nanoparticles around the evolved  $\text{H}_2\text{S}$  bubbles [27]. Cobalt hollow microspheres were synthesized via



**Fig. 4** SEM images of polyimides prepared by direct imidization process BPDA-DAT (a), and transimidization process BPDA-AP-DAT (b) at a concentration 1.5%



**Scheme 2** Schematic illustration for the preparation of hierarchical polyimide hollow spheres via a gas bubble template assisted transimidization induced crystallization process

aggregation of primary nanoparticles assisted by the gas bubbles liberated from the reaction [28]. However, most of works using gas bubbles as soft templates for the preparation of hollow spheres are focused on inorganic materials, and the preparation of polymer hollow spheres have been rarely reported. Based on a gas bubble templated mechanism, a plausible formation process of hierarchical polyimide hollow spheres in our research might be illustrated as follows: rightly after the two monomers were mixed at 350 °C, the solution became turbid immediately, which means the degree of polymerization of the oligomers quickly exceeded a critical value, and immediately precipitated from the solution to form polyimides nuclei, the nuclei then quickly grow into primary PI nanoparticles. At the same time, the transimidization between blocked dianhydride PMDA-AP and DAT resulted in polyimide by eliminating 2-aminopyridine (AP) as small molecule, because the reaction temperature is much higher than the boiling point of AP, thus it was volatilized and formed gas bubbles in the reaction solution. The in situ formed gas bubbles provide a heterogeneous nucleation center for newly formed crystalline polyimide nanoparticles which have a high surface energy due to their small diameter, so the primary PI nanoparticles trended to aggregate around the gas–liquid interface, thus gradually formed the hierarchical hollow microspheres composed of crystalline nanoparticles.

## Conclusion

In summary, hierarchical polyimide hollow microspheres consisting of crystalline nanoparticles were synthesized by a novel transimidization induced crystallization process. The formation process of hollow microspheres can be conceptualized in three steps based on the aggregation of primary crystalline PI nanoparticles on the in situ formed gas bubble templates: At the beginning of transimidization process, primary fine crystalline nanoparticles were formed through the transimidization induced crystallization of PI oligomers, the formed nanoparticles trend to attach at the gas/liquid interface of the in situ formed gas bubbles in order to minimize the surface energy, and thus formed the hierarchical hollow spheres. The use of in situ formed gas bubbles as soft templates provide a novel and effective method for the fabrication of high performance polymer hollow spheres; compared to the other



templated methods such as emulsion and silica spheres, this gas bubble template method is very simple, convenient and avoids the introduction of impurities. However, we must realize the mechanism behind the bubble template method is actually very complex, many factors, such as morphology of primary nuclei, surface properties of the nanoparticles, particle size, electrostatic interactions, etc., can affect the finally resulted morphology. Further studies are carrying on to further illustrating its mechanism and to the control of the hollow spheres, such as the sphere size, shell thickness, and functionalization of the high performance polymeric hollow spheres.

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