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Anomalous Polyimide Nanoparticles Prepared from Blending of Unlike Polymers

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Anomalous polyimide (PI) nanoparticles with controllable morphology, i.e., porous hollow structures, hollow structures, or bowl-like structures, were fabricated by blending a second polymer with poly(amic acid) (PAA, the precursor of PI) through the reprecipitation method and subsequent imidization. The phase separation between PAA and the porogen induced the formation of various hollow PI nanoparticles. The hollow morphology was mainly affected by the compatibility/interaction between PAA and the porogen. Hollow PI nanoparticles with superficial pores (ca. 30 nm), smooth surface, or holes in their surfaces can be obtained by selecting a suitable porogen, respectively.

Keywords: bowl-like nanoparticles; hollow nanoparticles; polyimide; polymer blend; porous hollow nanoparticles; reprecipitation method

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INTRODUCTION

The design and fabrication of polymer nanoparticles with various morphology have attracted a considerable amount of attention in recent years owing to their potential utility in controlled delivery systems, lightweight fillers, catalyst supports, confined reaction vessels, selective separation, electronics, optics, chromatography, and so on [1–5]. Hollow polymeric particles were mostly synthesized through the template-assisted emulsion/suspension polymerization. In these approaches, inorganic spheres [6–9], polymer particles [10,11], hydrocarbon solvents [12], and micelles [13,14] were employed as the template to form the hollow core. The core template was covered by one or more outer shells, and then the hollow particles were produced by removal of the core through dissolution or decomposition.

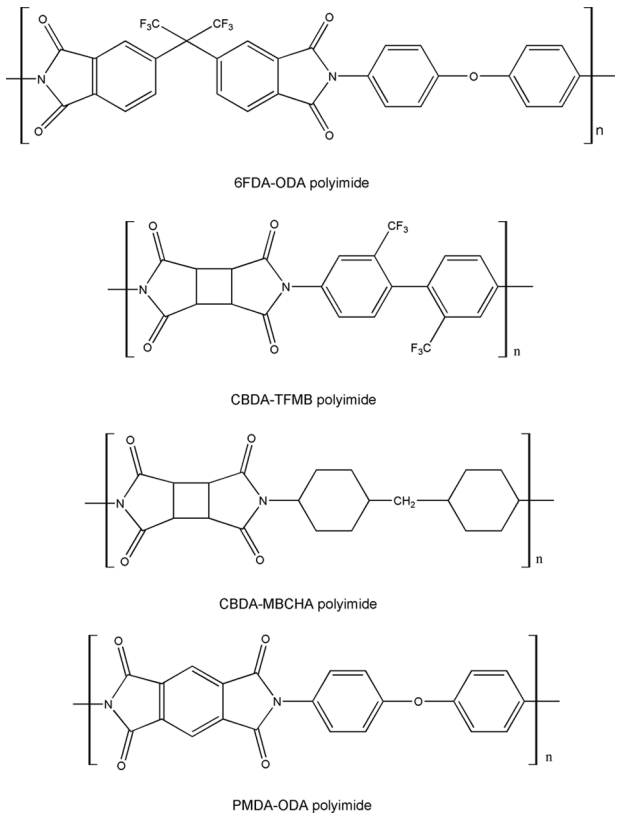
Polyimide (PI) is a representative high performance plastic and has been mostly employed as deposited films in the microelectronics industries, because of its great thermal stability, low dielectric constant, good adhesion to semiconductor, etc. [15,16]. As far as we are aware there are no reports about fabrication of PI nanoparticles with anomalous nanostructures (e.g., hollow nanoparticles with superficial pores on their surfaces). Such PI nanoparticles can provide many advantages for systems as interlayer insulators, biocompatible devices, and nano devices for optical communication [17–23]. Nevertheless, PI nanoparticles can not be synthesized through abovementioned emulsion/suspension polymerization.

Recently, we have reported [24,25] that porous PI nanoparticles possessing superficial pores with controlled thickness can be prepared using the reprecipitation method, with a second polymer as the porogen, and subsequent imidization of poly(amic acid) (PAA, precursor of PI). The porous PI nanoparticles were obtained through the imidization of the PAA nanoparticles, which were generated by injecting the PAA solution into a non-solvent (i.e., the reprecipitation process based on the different solubility of PAA in two different solvents). Such porous structures result from phase separation of PAA and the porogen in refined nanospace (i.e., individual composite nanoparticles). With regard to the diversity of polymer, it is considered that a simple and possible approach to prepare anomalous PI nanoparticles possessing various morphology is to select an alternative porogen by controlling the compatibility/interaction of PAA and the porogen. In the present paper, we demonstrated the fabrication of anomalous PI nanoparticles having different internal/superficial structures through the reprecipitation method and subsequent imidization.

EXPERIMENTAL

Materials

Four kinds of PIs were investigated (Scheme 1). The PAA precursor 6FDA-ODA [24], which had been synthesized from 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 4,4′-oxydianiline (ODA), was supplied by Nissan Chemical Industries. The PAA precursor CBDA-TFMB [26] was synthesized from 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and bis(2,2′-trifluoromethyl)benzidine (TFMB). The PAA precursor CBDA-MBCHA [27] was synthesized from 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and 4,4′-methylenebis(cyclohexylamine) (MBCHA). The PAA precursor PMDA-ODA, which had been synthesized from pyromellitic



SCHEME 1 Chemical structures of polyimide.

dianhydride (PMDA) and 4,4′-oxydianiline (ODA), was purchased from Aldrich. Poly(vinyl alcohol) (PVAL; $M_w = 10{,}000$; Aldrich), poly(vinyl pyrrolidone) (PVP; $M_w = 10{,}000$; Aldrich), poly(methyl methacrylate) (PMMA; $M_w = 15{,}000$; Aldrich), and polystyrene (PS; $M_w = 20{,}000$; Aldrich) were used as porogens without further purification. 1-Methyl-2-pyrrolidinone (NMP; the good solvent), cyclohexane (the poor solvent), pyridine (the catalyst), and acetic anhydride (the dehydrating agent) were purchased from Wako Pure Chemical Industries and used without further purification.

Preparation of Anomalously Shaped PI Nanoparticles

A mixed NMP solution of PAA and porogen was prepared in the manner described before [24,25]. The final concentration of PAA was 1.0 wt %; the ratio of added porogen to the amount of PAA varied from 0.1 to 1.0. In a typical reprecipitation method [28], a sample (100 μL) of the mixed NMP solution of PAA and porogen was injected via a microsyringe into vigorously stirred cyclohexane (10 mL) as the poor solvent at room temperature. The following two-step imidization [24,25] was performed to convert PAA to PI. After chemical imidization, the PI nanoparticles were separated using a centrifuge, dried *in vacuo*, and then thermally imidized at 270°C for 1 h, resulting in PI nanoparticles with various morphology.

Characterization

Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-6700 F instrument operated at an acceleration voltage of 15 kV and an emission current of 10 μA. Transmission electron microscopy (TEM) images were recorded using a JEOL JEM-2010 instrument operated at an acceleration voltage of 200 kV. One droplet of the anomalous PI nanoparticles dispersion liquid was applied to a 150-mesh carbon-coated copper grid and air-dried at room temperature.

RESULTS AND DISCUSSION

Porous PI nanoparticles with pores on their surfaces have been previously fabricated through adding poly(acrylic acid) (PAS) as the porogen to different PAA [24,25]. The porous structures result from phase separation of PAA and PAS within their composite nanoparticles during the reprecipitation process. The reasonable compatibility (but not too high) between the polymers induced pores and the degree of compatibility affected the depth of the pores. This strategy provides

a possible approach to prepare PI nanoparticles having various structures through controlling the compatibility between PAA and the porogen.

In present study, porous PI nanoparticles owning hollow cores were obtained using PVAL as a porogen. As shown in the SEM and TEM images (Fig. 1), the PI nanoparticles possessed not only superficial pores like what we previously reported [24,25], but also hollow cores inside. Interestingly, although the surface morphology of all PIs nanoparticles did not depend on PAA structures, the internal morphology was changed. In the case of CBDA-TFMB, the porous structure having a few hollow cores inside each nanoparticle was observed, while 6FDA-ODA porous nanoparticles gave the single hollow core, because PVAL is an even more compatible porogen for 6FDA-ODA than for CBDA-TFMB. The formation of such anomalous structures may be divided into two parts. One is the superficial area and the other is the central area. In the surface layer of the nanoparticles, PAA and PVAL phases separated due to the poor compatibility between PAA and PVAL. Subsequently, PVAL phases were eluted to generate the superficial pores as the way described before [24,25]. On the other hand, inside the nanoparticles, PVAL phase may remain because of possible inter-associated hydrogen bonds between PVAL and PAA/NMP [29].

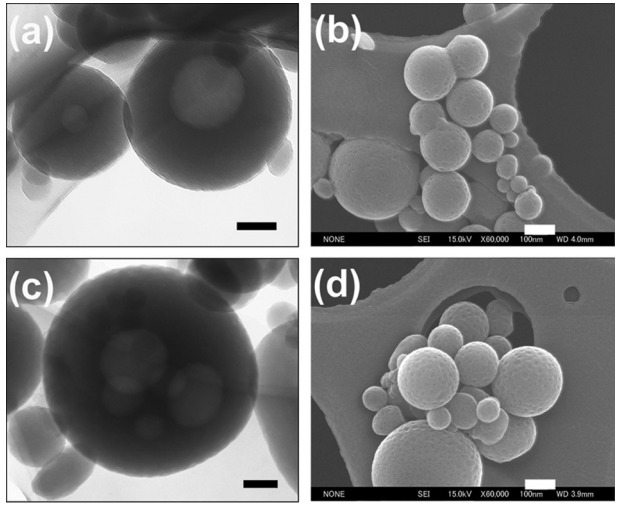


FIGURE 1 TEM and SEM images of porous PI nanoparticles having hollow cores prepared from different PAA using PVAL as the porogen at same content of 20 wt%: (a, b) 6FDA-ODA + PVAL; (c, d) CBDA-TFMB + PVAL. Scale bars in (a, c): 100 nm, scale bars in (b, d): 200 nm.

Finally, the pyrolysis of PVAL led to the formation of hollow cores. Clearly, the incorporation of specific interaction induced by the porogen provides the porous hollow structures of PI nanoparticles. Although the hydrogen bonds between different components within the composite nanoparticles are difficult to be measured, we can qualitatively estimate the compatibility between the two polymers from the non-hydrogen bonded solubility parameters (δ) of each component [30]. The smaller difference in the solubility parameters indicates that the polymers are more compatible. The solubility parameter is given by

$$\delta = \sqrt{\frac{E_{coh}}{V}}, \tag{1}$$

where E_{coh} is cohesive energy and V is molar volume. According to reference 30, E_{coh} value can be predicted by using a group contribution method, i.e., provided by a summation of E_{coh} of each group in a molecule. The value of polar groups is larger than that of non-polar groups. Namely, two kind of molecules consisting of similar groups tend to be compatible each other. However, since a compatibility is discussed by considering only the different of E_{coh} value, molecules possessing an ability of strong interactions, such as hydrogen bonding, are actually more compatible even if a different of E_{coh} is large. The combination of PVAL ($\delta_{\mathrm{PVAL}} = 30.5$) and 6FDA-ODA ($\delta_{\mathrm{6FDA\text{-}ODA}} = 20.8$) provided the nanoparticles with shallower superficial pore than that of PAS ($\delta_{\mathrm{PAS}} = 23.6$) and 6FDA-ODA in the previous study. This result means that higher compatibility between PAA and a porogen gives nanoparticles with deeper surface pores. In addition, it is considered that the high compatibility derived from hydrogen bonding gave hollow structure. Actually, in XPS measurement, shifts of O1s peaks of PAA and PVAL in these mixture have been found, indicating presence of hydrogen bonding between them.

Our approach is also applicable to other PIs. Multi-hollow PI(PMDA-ODA) ($\delta_{\mathrm{PMDA\text{-}ODA}} = 21.2$) nanoparticles were prepared by choosing PMMA ($\delta_{\mathrm{PMMA}} = 19.7$) or PVP ($\delta_{\mathrm{PVP}} = 19.9$) as the porogen, because of the closer values of δ. As shown in Figure 2, each PI nanoparticles have several independent cores rather than a big hollow core. But no pores were observed on their surfaces. High compatibility between PAA and the porogens led to the formation of hollow cores within each PI nanoparticles.

Interestingly, bowl-like PI nanoparticles were fabricated when we chose the combinations of CBDA-MBCHA ($\delta_{\mathrm{CBDA\text{-}MBCHA}} = 16.1$) and PS ($\delta_{\mathrm{PS}} = 17.9$)/PMMA ($\delta_{\mathrm{PMMA}} = 19.7$) (see Fig. 3). The formation mechanism for these nanoparticles is considered as follows. The

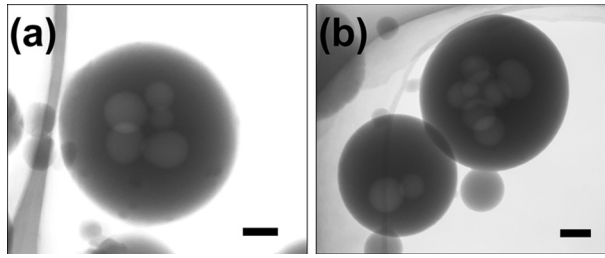


FIGURE 2 TEM images of hollow PI nanoparticles having independent cores within individual nanoparticles prepared using various porogens at same content of 20 wt%: (a) PMDA-ODA + PMMA; (b) PMDA-ODA + PVP. Scale bars: 100 nm.

generation of the nanoparticles by means of the reprecipitation method is finished within 1 s, thereby making the phase separation of PAA and the porogen occurs in a confined nanospace with existence of the solvent under nonequilibrium condition. Besides the compatibility and/or interaction between PAA and the porogen, effects of the solvents can not be neglected. In all abovementioned combination of PAA

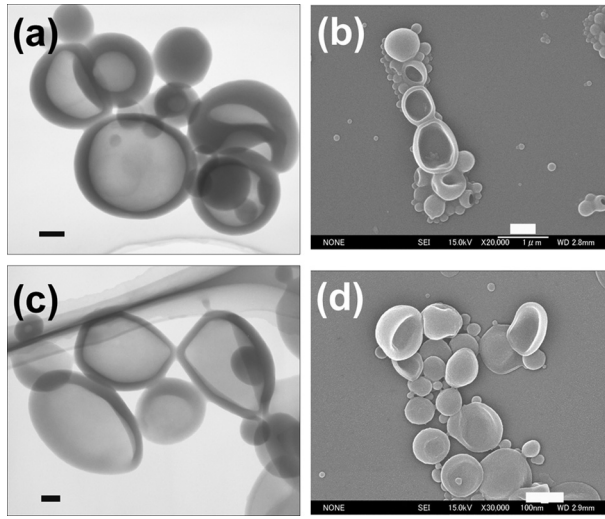


FIGURE 3 TEM and SEM images of bowl-like PI nanoparticles prepared using different porogens at same content of 20 wt%: (a, b) CBDA-MBCHA + PS; (c, d) CBDA-MBCHA +PMMA. Scale bars in (a, c): 100 nm, scale bars in (b, d): 500 nm.

and the porogen, both of them are more soluble in NMP (the good solvent; $\delta_{NMP} = 23.1$) than in cyclohexane (the poor solvent; $\delta_{cyclohexane} = 16.8$). CBDA-MBCHA and PS/PMMA, however, are more compatible to cyclohexane than to NMP. Thus, the mutual diffusion between cyclohexane and NMP did not promote the precipitation of PAA as it did in the combination of 6FDA-ODA and PAS [24]. Therefore, phase separation further progressed. According to the solubility parameters, cyclohexane is a much poorer solvent for PS/PMMA than for CBDA-MBCHA. PS/PMMA-rich phases formed within the composite nanoparticles. Before the complete precipitation of PAA nanoparticles, PS/PMMA phases were removed, leading to the generation of holes in the surfaces of PAA nanoparticles. As shown in Figure 3, the holes in the surfaces of hollow PI nanoparticles were larger when using PMMA as the porogen. Because PMMA is less compatible to CBDA-MBCHA, comparing with PS.

The selection of the combination of PAA and the porogen is the key factor for controlling the morphology of the PI nanoparticles. A suitable porogen can be determined qualitatively by regarding its solubility in the solvents, compatibility with PAA and molecular weight. The reasonable high compatibility of PAA and the porogen provides the various morphology of hollow PI nanoparticles. Moreover, specific interaction (e.g., hydrogen bonding) induced by the porogen can also influence the morphology. Thus, a choice of the porogen must be made by judicious consideration of all the aspects of the conditions.

CONCLUSIONS

Here, we demonstrated that our strategy provides a simple approach for fabricating hollow PI nanoparticles with various surface morphology through choosing a suitable polymer porogen. The selection of the reasonably compatible combination of PAA and the porogen resulted in the generation of hollow PI nanoparticles having from superficial pores to large holes in their surfaces. The hollow morphology was induced by phase separation between PAA and the porogen, which was influenced by the compatibility between PAA and the porogen. We expect that our strategy can be tuned and extend its applicability to other polymer systems.

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