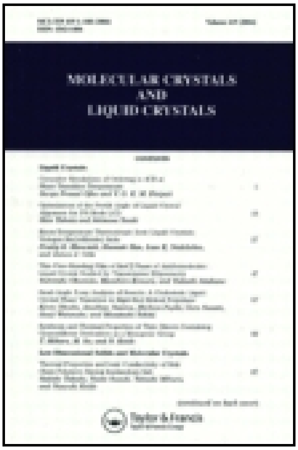

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PREPARATION OF POLYIMIDE ULTRAFINE PARTICLES

Masao Suzuki [a] , Hitoshi Kasai [b] , Hirohiko Miura [b] , Shuji Okada [b] , Hachiro Nakanishi [b] , Hidetoshi Oikawa [c] , Takayasu Nihira [d] & Hiroyoshi Fukuro [d]

[a] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

[b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan and CREST, JST(Japan Science and Technology Corporation)

[c] Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, 305-0047, Japan and CREST, JST(Japan Science and Technology Corporation)

[d] Electronic Materials Research Laboratories, Nissan Chemical Ind., LTD., Funabashi 274-8507, Japan and CREST, JST(Japan Science and Technology Corporation)

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PREPARATION OF POLYIMIDE ULTRAFINE PARTICLES

Masao Suzuki
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Hitoshi Kasai, Hirohiko Miura, Shuji Okada, and Hachiro Nakanishi
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan and CREST, JST(Japan Science and Technology Corporation)

Hidetoshi Oikawa
Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, 305-0047, Japan and CREST, JST(Japan Science and Technology Corporation)

Takayasu Nihira and Hiroyoshi Fukuro
Electronic Materials Research Laboratories, Nissan Chemical Ind., LTD., Funabashi 274-8507, Japan and CREST, JST(Japan Science and Technology Corporation)

Relationship between the size of Polyimide fine particles and some conditions in the reprecipitation method was investagatge. As a result, polyimide ultrafine particles with ca. 50 nm in size have been successfully fabricated through the "two-steps imidization", i.e. chemical imidization followed by thermal imidization of poly(amic acid) (PAA) precursor ultrafine particles prepared under an optimum reprecipitation condition.

Keywords: polyimide; poly(amic acid) precursor; reprecipitation method; two-steps imidization; ultrafine particles

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INTRODUCTION

Polyimide (PI), which is one of the most promising high-performance polymeric materials possessing highly thermal stability, good mechanical properties, easy processability, and low dielectric constants, is widely employed in the fields of microelectronics applications such as substrate of flexible printed circuitry boards, insulating layers in multilevel Very-Large-Scale Integrated (VLSI) circuits, buffer coatings in electronic package. Most of the studies on PI have been focused on films, adhesives, and varnish. PI seems to exhibit good physicochemical properties in particle forms, which could be used as the coating materials of insulating parts, low dielectric filler, and spacer for liquid crystal devices. However, few studies on preparation of PI nanoparticles have been carried out so far [1–3].

On the other hand, we have proposed the "reprecipitation method" as the simple technique to obtain various kinds of organic nanoparticles/nanocrystals with the range of size from several tens nanometer to sub-micrometer in the dispersion medium, and demonstrated its versatility [4–8]. Moreover, we have reported that these organic fine particles show novel properties which is different from those of the bulk materials and demonstrated the size effect of the properties [5,6,9]. In the case of PI fine particles, the specific size effects of its optical and electronic properties are also expected.

In the present article, we will report that PI ultrafine particles with *ca.* 50 nm in size have been successfully fabricated through the "two-steps imidization", i.e. chemical imidization followed by thermal imidization of poly(amic acid) (PAA) precursor ultrafine particles prepared by the reprecipitation method. These ultrafine particles were obtained by optimizing concentration of the injected solution and the kinds of poor solvents.

EXPERIMENTAL

Materials

PAA used as a precursor polymer was produced by polyaddition reaction of 4,4′-oxydianiline (ODA) and 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) in N-methyl-2-pyrrolidinone (NMP), and the average molecular weight (M_w) and polydispersity (M_w/M_n) of PAA are summarized in Table 1. The chemical structures of PAA and the corresponding PI are shown in Figure 1.

Preparation of PAA Fine Particles by the Reprecipitation Method

PAA fine particles were prepared by the reprecipitation method [4–8]. Namely, 100 μl of NMP solution of PAA was rapidly injected into a vigorously

TABLE 1 Average Molecular Weight and Polydispersity of PAA

Sample Code	M_w	M_w/M_n
PAA1	4.5×10^4	2.86
PAA2	6.9×10^4	1.84
PAA3	9.3×10^4	1.70
PAA4	1.2×10^5	1.66

stirred poor solvent (10 ml) using a microsyringe. In our case, three kinds of poor solvents were used : carbon disulfide (CS_2), cyclohexane, and their mixture (the misciblility for NMP : cyclohexane < mixture < CS_2). In fact, the solubility parameters of NMP, CS_2, and cyclohexane calculated by Hansen method [10] were 22.9 $MPa^{1/2}$, 20.5 $MPa^{1/2}$, and 16.8 $MPa^{1/2}$, respectively, and the difference in solubility parameter, which are often used for evaluating the miscibility between two kinds of solvents, is much lower for NMP/CS_2 system than that of NMP/cyclohexane system. A small amount of the dipersing agent, Acrydic A-1380 (DAINIPPON INK AND CHEMICALS), was added into poor solvent before injection to suppress the aggregation of fine particles. The PAA fine particles were successfully obtained immediately after injection as white dispersion in poor solvent. All solvents were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification.

In general, the particle size and the morphology could be easily controlled by varying the reprecipitation condition such as concentration of the injected solution, temperature, surfactant, solvent species and mixing methodlogy. In the present case, the concentration of the injected solution (C), solvent species was important. In addition, the particle size was influenced by molecular weight (M_w) of PAA in our case. Particulaly, C and solvent species were effective for reducing the size of PAA fine particles until below 100 nm. Thus, the reprecipitation conditions were changed as follows : C, the volume ratio (Φ) of CS_2 in the CS_2/cyclohexane mixture and M_w were changed as follows : $C = 0.04-1.9$ wt% in PAA-NMP solution, $\Phi = 0$–1, $M_w = 4.5 \times 10^4$–12.0×10^4. In any case, both temperature of poor solvent and injection solution were constant at 22°C.

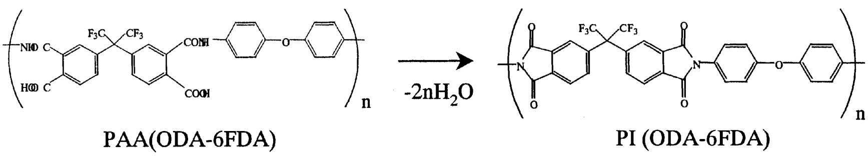

FIGURE 1 Chemical structures of PAA and the corresponding PI.

Preparation of PI Fine Particles

PI fine particles were prepared through the "two-steps imidization", i.e. chemical imidization followed by thermal imidization of poly(amic acid) (PAA) fine particles. Chemical imidization of PAA nanoparticles was performed by adding 100 μl of pyridine/acetic anhydride mixture (1 : 1) into the PAA nanoparticles dispersion liquid [11]. After the chemical imidization, the resulting PI fine particles were centrifuged and dried *in vacuo*. Finally, PI nanoparticles were further cured at 270°C for 1 hr under nitrogen atmosphere to promote completely conversion to PI. After the two-steps imidization, almost quantitative conversion from PAA to PI was confirmed by IR spectra (not shown). The PAA and PI fine particles were characterized by scanning electron microscope (SEM), dynamic light scattering (DLS) measurement.

RESULTS AND DISCUSSION

Morphology of PI Nanoparticles

We have successfully prepared the PAA nanoparticles, ranging from several tens to hundreds of nanometers in size by varying C. The fine particles dispersions were slightly turbid due to light scattering. The mean particle size and size distribution were almost maintained even after the two-steps imidization in any conditions [11]. Figure 2 indicates the SEM photograph of typical PI fine particles prepared by reprecipitating into cyclohexane(mean size: *ca.* 100 nm). PI fine particles prepared were all spherical and this morphology was hardly influenced in any reprecipitation conditions.

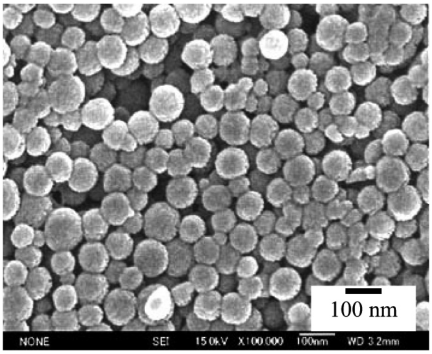

FIGURE 2 SEM photographs of typical PI fine particles. Reprecipitation conditions: PAA4, $C = 0.32$ wt%, $\Phi = 0$.

Size Control of PAA Fine Articles

Figure 3 shows the relationship between *C* and the particle size of PAA fine particles. When *C* was too high in any case, the precipitation macroscopically occurred just after injecting PAA-NMP solution. In a word, the concentration ranges in Figure 3 was the suitable one to obtain stably PAA fine particles dispersion. This threshold concentration to avoid macroscopic precipitates was lowered with increasing M_w. The lower limit of concentration range was set at 0.2 wt% in any M_w. As shown in figure, it has become apparent that the particle size decreased monotonously with decreasing *C*, and this tendency became clearly remarkable with increasing M_w of PAA. On the whole, the size of PAA fine particles, namely that of PI fine particles, was found to be controllable between *ca.* 100–300 nm by varying *C* from 0.2 to 1.9 wt%.

From these results, particle size should be reduced by using further diluted solution. Actually, when *C* was set at 0.05 wt% for PAA4-NMP system, PI ultrafine particles with *ca* 50 nm in size was successfully

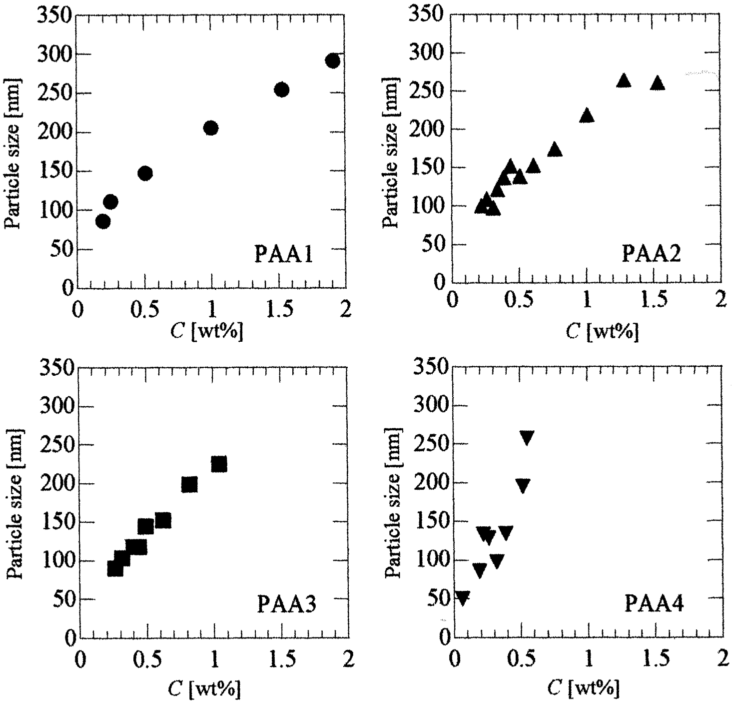

FIGURE 3 Relationship between *C* and particle size. In any M_w, reprecipitaition was performed at $\Phi = 0$.

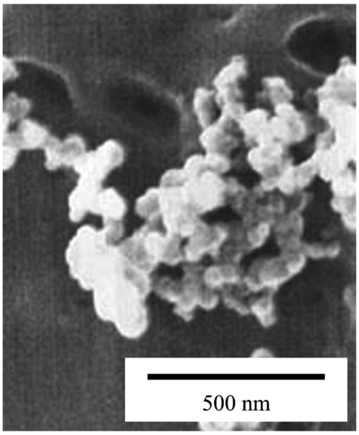

FIGURE 4 SEM photograph of PI ultrafine particles. Reprecipitation conditions : PAA4, $C = 0.05$ wt%, $\Phi = 0$.

obtained by reprecipitating into cyclohexane (Figure 4). However, when further diluted solution was used, it was difficult to evaluate the size by DLS and SEM because of the low yield, though ultrafine PI particles with ca. 28 nm in size were identified only by DLS when C was set at 0.04 wt%.

On the other hand, it was found that ultrafine particles with *ca.* 50 nm in size by using CS_2 as poor solvent even when concentration range was relatively high. Figure 5 shows the dependence of the size of PAA2 fine particles on Φ at different C. As shown in figure, the particle size gradually decreased with increasing Φ. When Φ was unity, namely, the poor solvent

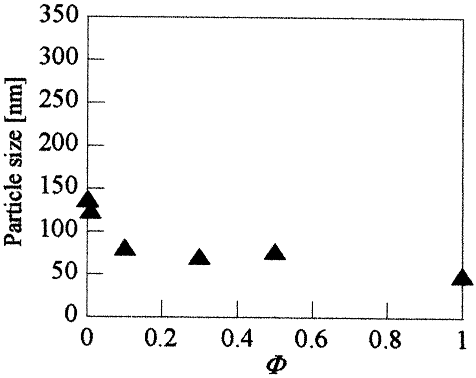

FIGURE 5 Dependence of the particle size of PAA2 nanoparticles on Φ. $C = 0.5$ wt%.

was pure CS_2, PAA nanoparticles with the size of *ca.* 50 nm were interestingly obtained, even if C is different in figure, and spherical PI ultrafine particles were confirmed by SEM observation. These results suggest that the formation mechanism of PAA fine particles should strongly depend on the miscibility between good and poor solvent.

CONCLUSION

We have demonstrated successfully a new approach for the preparation of PI ultrafine particles with ca. 50 nm in size. Namely, PAA ultrafine particles were first prepared by the reprecipitation method, and then converted to the corresponding PI ultrafine particles through the two-steps imidization : chemical imidization, and the subsequent thermal imidization. It was suggested that these ultrafine particles could be obtained by diluting the injected solution or by raising the miscibility between good and poor solvent in the present reprecipitation process.

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