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Green Synthetic Method and Simple Size-control of Polyimide Nanoparticles in $ScCO_2$

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A green method has been developed for the syntheses of polyimide nanoparticles (PI NPs) at high pressure in supercritical carbon dioxide ($scCO_2$) instead of conventional organic solvent. Without any complicated separation process, PI NPs can be obtained by depressurization of CO_2. This method allows preparation of size-controlled PI NPs (a few nm to 194 nm) simply by varying the temperature at a fixed pressure of CO_2.

Polyimide (PI) is a superengineering plastic and mostly used for deposited films in microelectronic applications such as flexible printed circuits (FPC), tape automated bonding (TAB), and buffer coatings in electronic packages. Especially, PIs have many excellent properties in terms of thermal, chemical, and mechanical durability, good adhesion to semiconductors, and low dielectric constant ($k = 2.4$ to 3.0 at present).[1]

PIs are among the most promising materials for interlayer dielectric phase (insulator),[2] especially for harsh manufacturing processes of next-generation semiconductor chips such as microprocessing units (MPUs) and dynamic random access memories (DRAMs) due to far better k values than carbon-doped silica ($k = 3.3$), which records the lowest value among the silicon compounds.[3] Nevertheless, these values are still too high to meet criteria (less than 2.0) required for the use of interlayer dielectric phase into ultra-large-scale integrated circuits.[2]

Several approaches have been developed to obtain PI with lower k value than 2.0. In view of the low dielectric constant of air ($k = 1.0$), incorporation of air voids has been envisioned as the most promising method, and decreasing the k values to 2.27 has been achieved.[4] Recently, we reported the synthesis of polymer particles focused on the precise controlling of morphologies and size in the range of submicrometer. We also proposed a novel strategy, which is to assemble ultra low-k PI films ($k < 2.0$) by electrophoretic deposition of newly fabricated porous PI nanoparticles (PI NPs).[5] Although our strategy can successfully developed materials with remarkably low k value (ca. 1.9), still large amounts of organic solvent such as cyclohexane is required for PI NPs production.[6]

Various alternative solvent media such as water, supercritical carbon dioxide ($scCO_2$),[7a] poly(ethylene glycol),[7b] and ionic liquids[7c] have been reviewed for a variety of material syntheses. Among them, $scCO_2$ as an environmentally benign solvent for material syntheses has significant advantages such as tunable density, which enables the medium to dissolve precursors. Furthermore, low viscosity and high diffusivity lead to particle deposition within confined geometries. In addition, $scCO_2$ is easy to handle because it is nonflammable, nontoxic, inexpensive, and readily available.[7a]

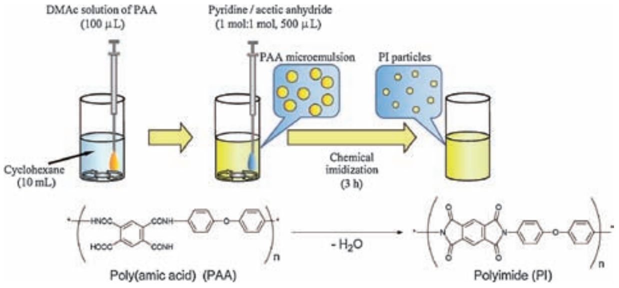

Figure 1. The formation of PI NPs with two-step process.

Figure 1 illustrates the formation of PI NPs in two steps using the conventional organic solvent, cyclohexane. At first, *N*,*N*-dimethylacetamide (DMAc) solution of poly(amic acid) (PAA) was injected using a microsyringe into cyclohexane with vigorous stirring to form a dispersion of PAA NPs. Then, a mixture of base (pyridine) and dehydrating reagent (acetic anhydride) was injected again to mediate the chemical imidization from PAA to polyimide (PI).[6] The particle size was defined at the first step, thus, when cyclohexane can be replaced by $scCO_2$, less organic solvent is required. Therefore, one might expect to control the particle size related to the emulsion size by fine tuning of solvent properties such as pressure and temperature. Furthermore, PI NPs would be obtained easily by depressurizing CO_2 without centrifuging using large amounts of organic solvents and long drying treatments.

First, we applied GAS (Gas Anti-Solvent) precipitation to prepare PI NPs with high-pressure and supercritical CO_2.[8] This process is simple and recently widely studied especially in the pharmaceutical industry for the micronization of various organic compounds.[9,10] The experimental procedure is as follows: A 50-mL high-pressure stainless steel vessel was placed in a hot air circulating oven. After the vessel attained the required temperature, a solution of *N*,*N*-dimethylacetamide (DMAc) of poly(amic acid) (PAA), acetic anhydride, and pyridine were introduced into the reactor vessel using a syringe, and then CO_2 was charged into the reactor using a high-pressure liquid pump. After the desired pressure was achieved, imidization was started with vigorous stirring by magnetic stirrer for 2 h. Finally, the pressure was released from the valve, and then the yellow residue in the vessel was washed with a small amount of cyclohexane (3 mL) three times with centrifuge and then dried under reduced pressure. Figures 2a and 2b show the SEM image of obtained PI NPs and corresponding size-distribution at 40 °C and 10 MPa, respectively. The image indicates that PI NPs are spherical. From the DLS measurement, 24% of CV value of size distribution was obtained.

FT-IR spectra of PI NPs prepared at 40 °C and a quantitatively imidized bulk film are shown in Figure 3. The spectrum of PI NPs corresponds well with that of the bulk film. The conversion degree of imidization to PI (PI(%)) can be given by the following equation with respect to the observed spectra,

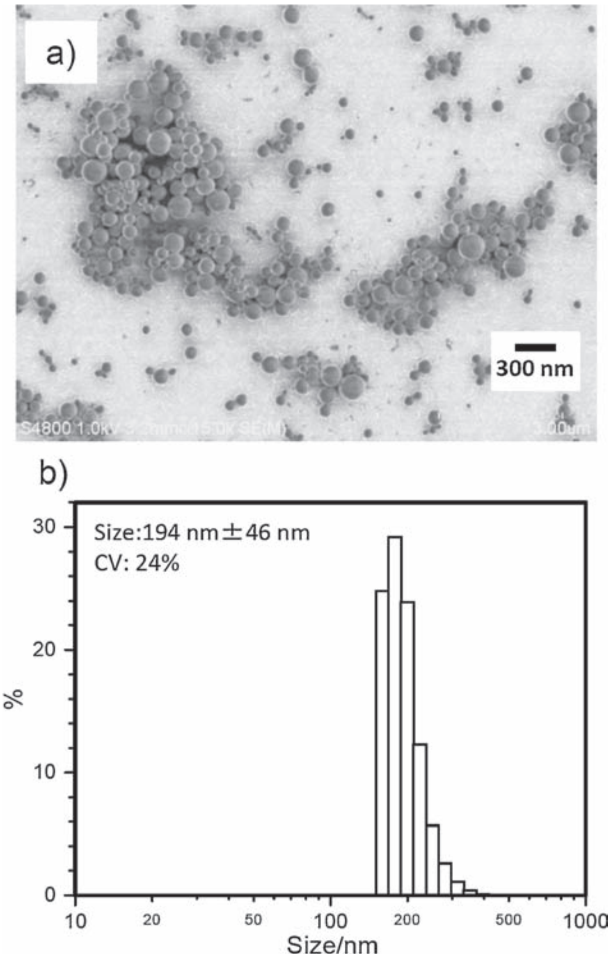

Figure 2. a) SEM image of PI NPs and b) particle size-distribution of PI NPs prepared in this study by DLS mesurement.

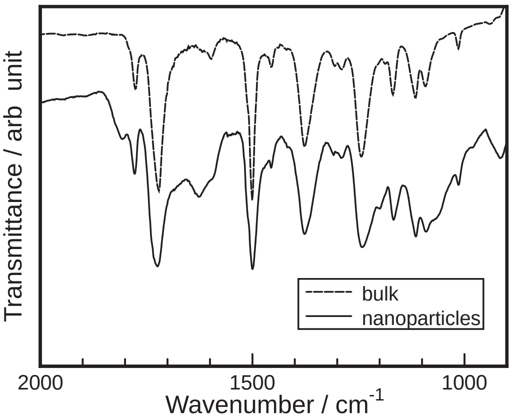

Figure 3. IR spectra of bulk film of PI (dashed line) and PI NPs fabricated at 40 °C (solid line).

$$\mathrm{PI}(\%) = \left(\frac{D_{1375\,\mathrm{cm}^{-1}}}{D_{1500\,\mathrm{cm}^{-1}}}\right)_{\text{nanoparticles}} \Bigg/ \left(\frac{D_{1375\,\mathrm{cm}^{-1}}}{D_{1500\,\mathrm{cm}^{-1}}}\right)_{\text{bulk}} \qquad (1)$$

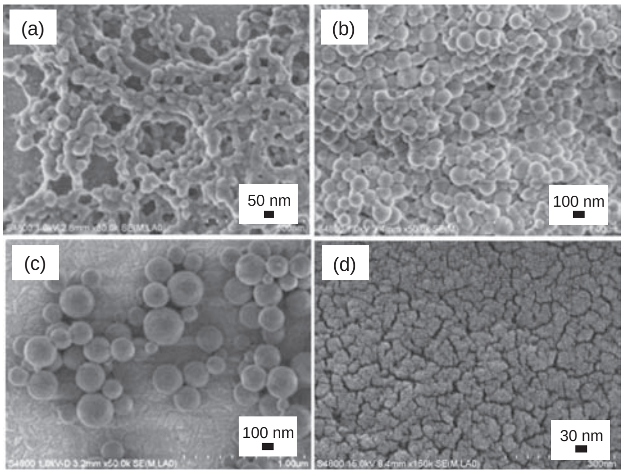

Figure 4. SEM images of PI nanoparticles fabricated at a) 20, b) 30, c) 40, and d) 50 °C.

where D is the optical density of each absorption band in IR spectra. The absorption bands at 1375 and 1500 cm^{-1} are attributed to C–N stretching vibration of imide ring and C–C stretching vibration of benzene ring, respectively. The band at 1500 cm^{-1} can be used as an internal standard because the number of benzene ring in PAA and PI molecule coincides accurately regardless of the conversion. From the Figure 3, the conversion degree of the nanoparticles prepared at 40 °C is calculated as 100%. On the contrary, 73% conversion was obtained when imidized in cyclohexane with acetic anhydride and pyridine as cyclodehydration reagents. The conversion of NPs prepared in CO_2 medium is higher than that in cyclohexane. This implies that the imidization rate must be accelerated under $scCO_2$.[7a,8] Therefore, this preparation method of PI NPs using $scCO_2$ instead of cyclohexane can provide an effective and more environmental friendly method than the former.

To investigate the formation of PI NPs in CO_2, phase behaviors of DMAc with CO_2 at 20 and 40 °C were studied in a 50-mL high-pressure view cell fitted with quartz windows.[11] In the lower pressure region of CO_2 (1 MPa), binary phase consisting of a liquid DMAc and CO_2 phase were observed at 20 and 40 °C. When the pressure was increased up to 10 MPa at 20 °C, liquid DMAc phase absorbed CO_2 and its volume increased. Finally, over 10 MPa, the vessel was filled with a liquid phase. In contrast, at 40 °C, DMAc was absorbed into a CO_2 gas phase. Increasing CO_2 pressure, volume of DMAc phase decreased and a single phase was formed. Thus, formation of PI NPs at 40 °C and 10 MPa occurred when the DMAc and CO_2 was mixed completely and gave a single phase.[12]

To clarify the formation of PI NPs in CO_2, we further investigated the effect of reaction temperature on the particle size with constant CO_2 pressure of 10 MPa. Figure 4 shows the SEM images of PI NPs obtained at various temperatures of 20, 30, 40, and 50 °C. Results revealed that the particle size increased from 61 to 194 nm with increasing temperature up to 40 °C. At 50 °C, the size was drastically decreased to a few nm[11] which can be explained by the phase behavior between a gas–liquid biphase and a single phase in supercritical state. When the temperature was below 40 °C, imidization occurred in liquid phase along with formation of PI micelles or metastable state. The size of PI micelles would be increased with increasing the content of CO_2 in liquid DMAc phase. It has to be mentioned that turbidity of liquid phase observed become higher with increase in temperature up to 40 °C after the formation of PI NPs, which reflect the formation of larger particles dispersed in liquid phase and obstructing the transmittance of light. When the temperature is over 40 °C, the turbidity of supercritical phase was much lower than that at 20 °C. In this state, free PI molecules or PI monomers with small aggregation number were formed in the supercritical phase.[13]

We also evaluated a layered film of the PI NPs prepared at 40 °C by conventional method.[5a] It's k value is 2.56 at 1 MHz and porosity calculated from the k value is 21%, which is closely resembles with previous value.[5a] Therefore, this method can be applied as a greener, effective preparation.[11–13]

In summary, PI NPs were prepared successfully using GAS. The described method is green and effective in comparison with the previous described process using conventional organic solvent. In addition, it is easy to control the particle size by tuning CO_2 state with pressure and temperature manipulation.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html. The exact particle size of Figure 4d could not determine by SEM observation. Figure S1: Phase behavior of DMAc solution of PAA + acetic anhydride + pyridine/CO_2 system at 20 and 40 °C; Figure S2: SEM image of the film coated by PI NPs prepared by the method under $scCO_2$ condition at 40 °C.

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