

# Synthesis of Polyimide Microparticles by Dispersion Polymerization

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**ABSTRACT:** We synthesized polyimide (PI) microparticles by a reaction between benzophenone-3,3,4,4-tetracarboxylic dianhydride and 4,4'-diaminodiphenyl ether using polyvinylpyrrolidone as a dispersant in four different organic solvents, at different temperatures, with different amounts of the dispersing agent, and with different concentrations of monomers. After dispersion polymerization, PI microparticles in the size range 200–800 nm were obtained. Absorptions at 1775 and 1720  $\text{cm}^{-1}$ , due to the C=O group of PI, and at 1375  $\text{cm}^{-1}$ , caused by the stretching vibration of the C–N group due to a lactam ring, were observed in

the IR spectrum, which suggested the successful synthesis of PI particles. Scanning electron microscopy analysis of microparticle morphology showed that the PI particle sizes increased with increasing temperature, concentration of dispersant, and concentration of monomers. In addition, the thermal stability is also discussed on the basis of the results of simultaneous Differential Scanning Calorimetry Modulated TA Instruments (DSC–TA) measurement. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3671–3675, 2009

**Key words:** particle size distribution; polyimides; TEM

## INTRODUCTION

Polyimides (PIs) are widely used in electrical industry, as electronic and automotive materials, and as alternatives for metal and/or ceramics because they have excellent mechanical properties and strong heat and solvent resistance and provide good insulation.<sup>1</sup> The synthesis of PIs is generally a two-step process: the first step is the polymerization of poly(amide acid) in a strongly polar solvent, such as dimethyl sulfoxide, at 70°C with anhydride and diamine; then, the system temperature is increased to more than 150°C to promote the amidation of poly(amide acid) into a PI.<sup>2–6</sup>

Dispersion polymerization is often used to synthesize polymer microparticles from vinyl monomers.<sup>7–9</sup> The polymerization system is initially a homogeneous solution; that is, the monomers, initiator, and stabilizing agent are all dissolved in a solvent, but the product polymer must not be soluble in the solvent, and the stabilizing agent, product polymer, and solvents must have affinity. After polymerization occurs, the initiator decomposes and reacts with the monomers in the solvent. When the product polymer chain is longer than a critical length, it is precipitated from the solvent and forms a nucleus. A number of nuclei aggregate to form a stable microsphere, and the stabilizing agent is adsorbed on the surface of the micro-

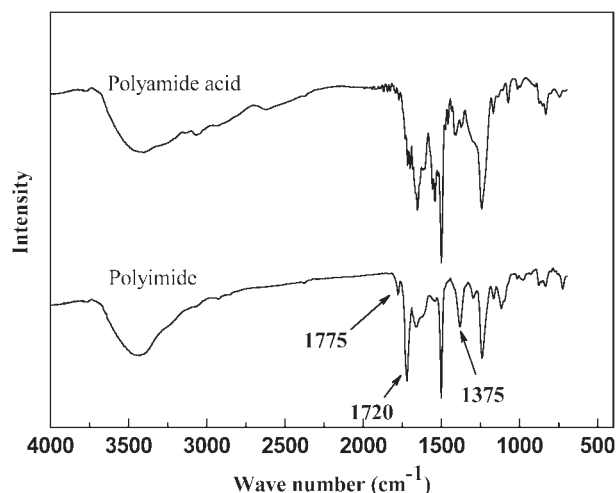
spheres to make the microspheres stable. Finally, the microspheres are formed by absorption of the monomers and initiator from the solvent, and polymerization occurs; that is, the polymerization moves from the solvent to the microspheres system.

A literature survey showed that no synthesis of PI microparticles with dispersion polymerization has been reported. In this article, we wish to report a new method for the synthesis of PI microparticles with dispersion polymerization in several organic solvents under different conditions. In addition, the properties of the product PI microparticles also were analyzed by IR spectroscopy, scanning electron microscopy (SEM), and simultaneous DSC–TA (SDT) measurements.

## EXPERIMENTAL

Polyvinylpyrrolidone (PVP), 4,4'-diaminodiphenyl ether (DPE), benzophenone-3,3,4,4-tetracarboxylic dianhydride (BTDA), methanol, ethyl acetate, methyl acetate, acetone, and xylene of analytical grade were obtained from commercial sources and used without further purification. A JSM-6700F scanning electron microscope (Jeol Co., Ltd., Tokyo, Japan) was used to examine the surface morphology of the PI microparticles. The thermal stability of the PI microparticles was determined by SDT (SDT Q600, Grimsby, Canada). The oven temperature was programmed to rise at a rate of 10°C/min from 25 to 900°C with nitrogen as the protection gas with a flow rate of 100 mL/min.

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**Figure 1** IR spectra of the (A) poly(amide acid) particles and (B) PI particles.

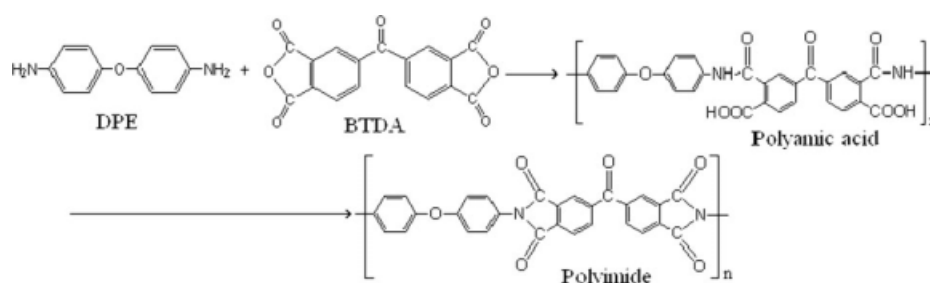
### Synthesis of the PI microparticles

The solvent (100 mL) and PVP as the quantitative dispersant were added to a 250 mL, three-necked flask and stirred, and after the PVP was dissolved, DPE and BTDA were added in quantitative order to the flask. After the reaction proceeded at 200 rpm for 24 h, the product was filtered and washed. A kind of poly(amide acid) particle was obtained, and the product was filtered, washed, and dried. The poly(amide acid) particles were dispersed in xylene and heated to over 150°C for 4 h to promote the imidization of poly(amide acid) particles into PI particles.

## RESULTS AND DISCUSSION

Many factors, such as temperature, stirring speed, polarity of the solvent, dispersing agent, and reaction monomer concentration affected the performance and morphology of the PI particles. In this study, dispersion polymerization between BTDA and DPE was used with stirring at 200 rpm. The effect of the solvent, reaction temperature, concentration of PVP, and concentration of reaction monomer are discussed in detail.

The chemical reaction equation of PI was as follows:



The PI particles obtained were analyzed by Fourier transform infrared measurement, as shown in Figure 1. Absorptions at 1775 and 1720  $\text{cm}^{-1}$  due to the C=O group of PI and at 1375  $\text{cm}^{-1}$  due to the C–N group between the imide rings and the adjacent phenyl<sup>10</sup> were observed; this suggested that the poly(amide acid) particles changed into PI particles.

### Effect of the solvent

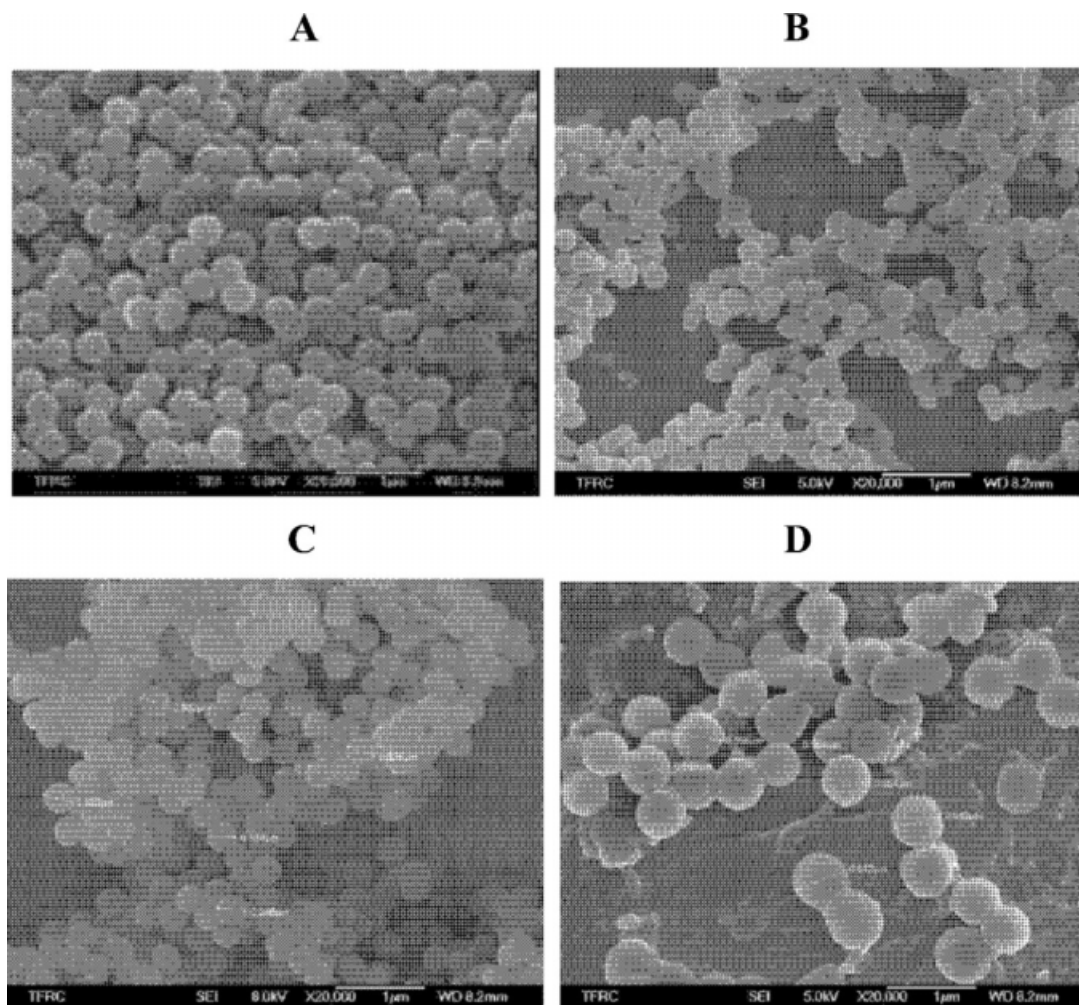
Four kinds of organic solvents were used as reaction solvents in this study, and the SEM photographs in Figure 2(A–D) show the reaction systems with acetone, methanol, ethyl acetate, and methyl acetate, respectively.

Spherical microparticles were obtained in all four solvents, and the average diameters of the microparticles calculated from Figure 2 were 380 nm in acetone, 280 nm in methanol, 330 nm in ethyl acetate, and 560 nm in methyl acetate. The diameter of the microparticles did not seem to be directly related to the polarity of the solvent in this study, and the biggest particles were produced with methyl acetate as the solvent.

### Effect of the temperature

Figure 3 shows SEM photographs of PI microparticles obtained at different reaction temperatures in methanol. The microparticles shown in Figure 3(A–C) were reacted at 0, 20, and 40°C, respectively.

As the reaction temperature increased from 20 to 40°C, the PI particles increased in size from 200–300 to 300–450 nm [Fig. 3(B,C)]. This was because, with increasing reaction temperature, the solubility of BTDA and DPE in methanol increased, and the reaction rate was accelerated. At the higher temperature, the reaction in the primary stage of poly(amide acid) quickly formed a nucleus and accumulated, and this was conducive to the formation of microparticles. At 0°C, no independent polyamide microparticles were obtained [Fig. 3(A)]. DPE and BTDA were hardly soluble in methanol at low temperatures; this slowed the formation of poly(amide acid) and extension and hampered the formation of the microspheres.

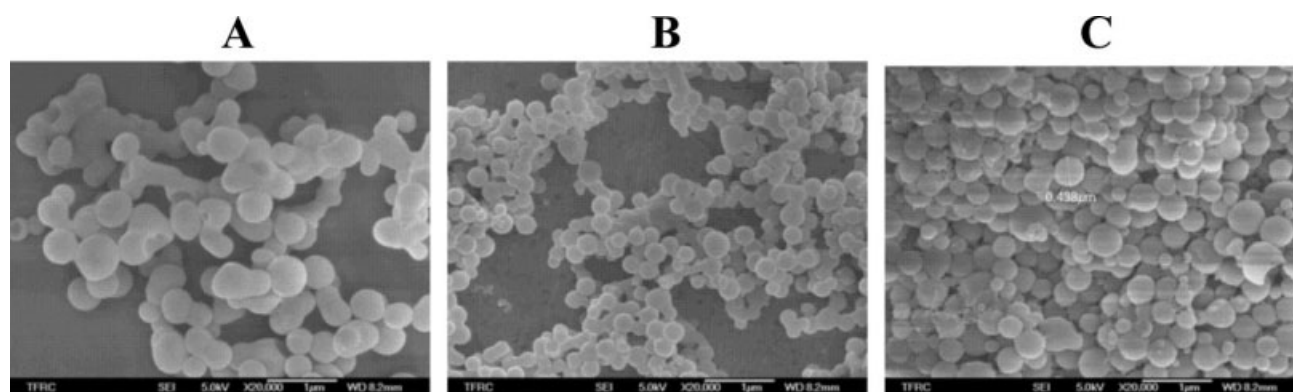


**Figure 2** SEM photos of PI microparticles prepared with different solvents: (A) acetone, (B) methanol, (C) ethyl acetate, and (D) methyl acetate.

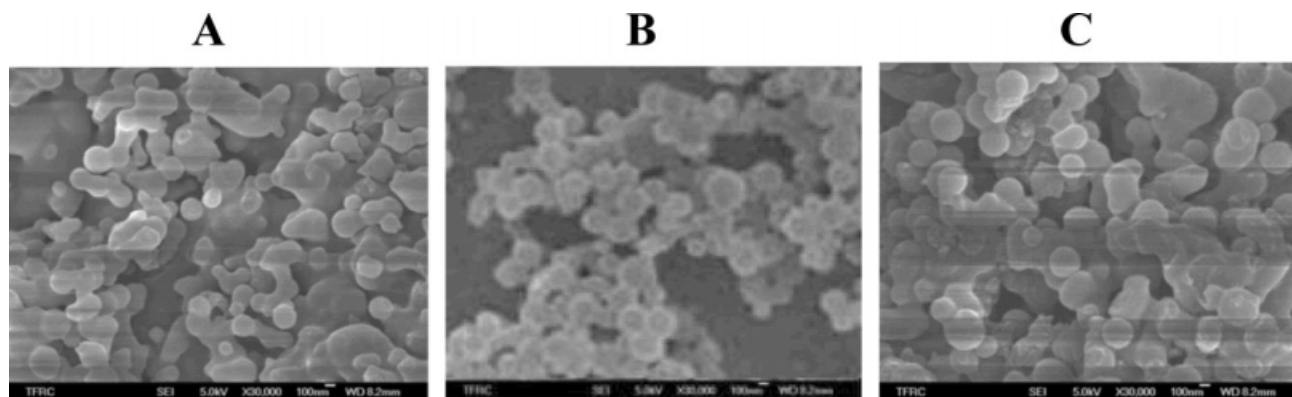
#### Effect of the amount of dispersant

Figure 4 shows the SEM photographs of the PI microparticles reacted in methanol with different amounts of dispersant. The amounts of PVP used for the PI microparticles shown in Figure 4(A–C) were 0.2, 0.5, and 1.0 g, respectively.

When the amount of PVP was increased from 0.2 to 0.5 g, the diameter of the PI particles increased from 200 to 300 nm [Fig. 4(A,B)]. Because of the increase in PVP, the poly(amide acid) nuclei generated were evenly dispersed in PVP, which effectively prevented aggregation of the poly(amide acid) particles.



**Figure 3** SEM photos of PI microparticles prepared at different temperatures: (A) 0, (B) 20, and (C) 40°C.



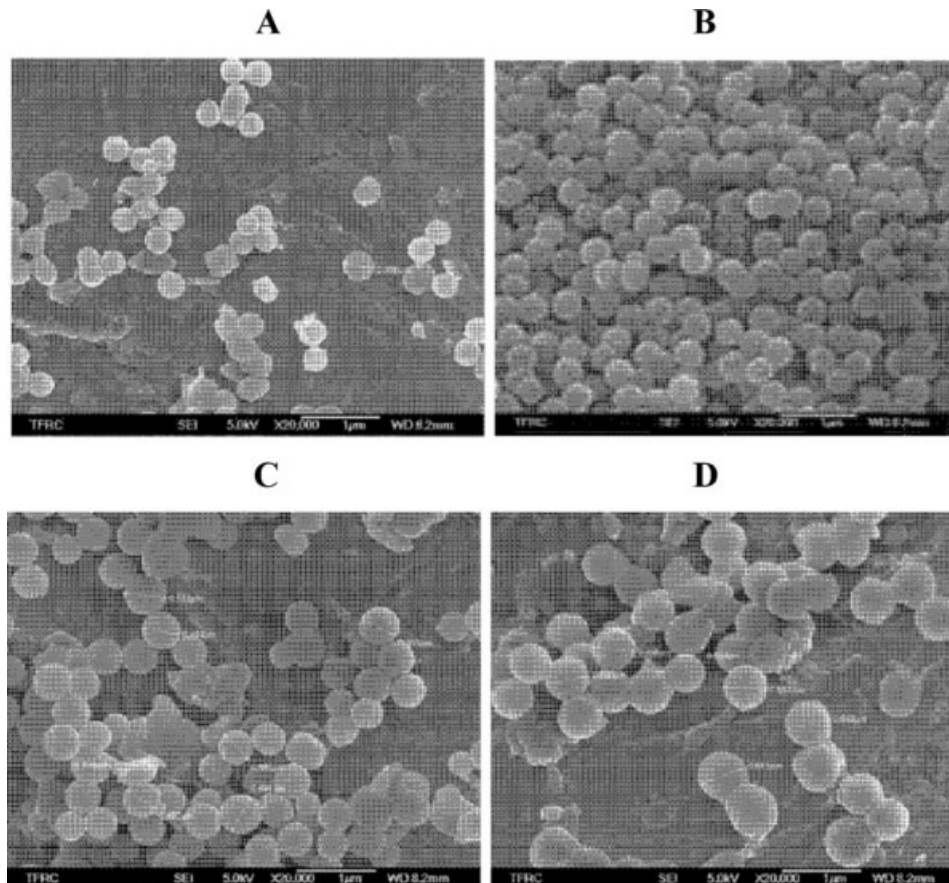
**Figure 4** SEM photos of PI microparticles prepared with different PVP amounts: (A) 0.2, (B) 0.5, and (C) 1.0 g.

However, when the amount of PVP increased from 0.5 to 1.0 g, aggregation was observed [Fig. 4(C)]. This may have been because high concentrations of PVP allowed BTDA to accumulate easily on the molecular surface of PVP while the DPE and BTDA reaction occurred, and the constantly expanding accumulation of poly(amide acid) leading to the next step of PI treatment produced some aggregation of PI microparticles.

#### Effect of the concentration of monomer

Figure 5 shows SEM photographs of PI microparticles with different concentrations of monomer. Figure 5(A–D) shows the concentration of DPE and/or BTDA monomers at 0.001, 0.002, 0.005, and 0.01 mol, respectively.

When the concentration of monomers increased, the diameter of PI particles also increased from 330 nm



**Figure 5** SEM photos of PI microparticles prepared with different concentrations of monomer: (A) 0.001, (B) 0.002, (C) 0.005, and (D) 0.01 mol.

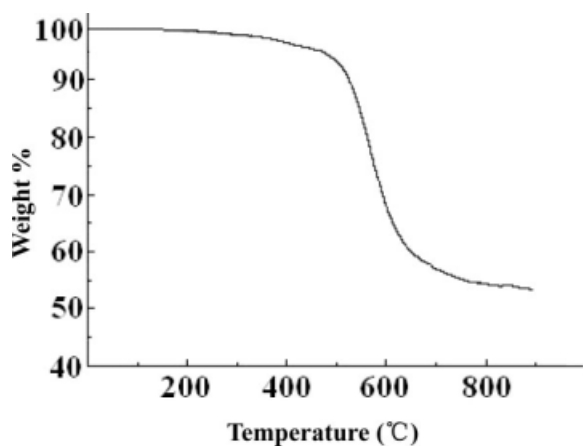


Figure 6 TGA curve of the PI microparticles.

[Fig. 5(A)], 380 nm [Fig. 5(B)], and 475 nm [Fig. 5(c)] to 560 nm [Fig. 5(D)], respectively. As the concentration of monomers increased, the generation of poly(amide acid) nuclei and their aggregation became easier, and the diameter of the particles increased.

#### Thermal stability

The thermal stability of the PI microparticles was analyzed with SDT, and the results are shown in Figure 6. The weight was slightly reduced under 500°C, and this could have been due to the loss of volatile organic solvents contained in the sample. When the temperature was over 515°C, a sharp decline that meant the beginning of decomposition of the sample occurred.

#### CONCLUSIONS

In this study, we successfully synthesized PI microparticles by dispersion polymerization; this was confirmed by IR measurement. With characterization by SEM and SDT measurements, the results show that the solvent environment, temperature, amount of dispersant, and concentration of monomers strongly affected the diameter of the particles. In the synthesis conditions of 0.5 g of dispersant, 0.002 mol of monomers, and dispersion polymerization in methanol at 20°C, spherical PI microparticles with diameters from 200 to 300 nm were obtained. The thermal decomposition temperature of the PI microparticles was over 500°C according to the SDT measurement.

#### References

1. Ma, G. H.; Su, Z. G. *Polymer Microsphere Material*; Chemical Industry Press: Beijing, 2005.
2. Kasai, H.; Oikawa, H.; Nakanishi, H.; Okada, S.; Suzuki, M. *Jpn. Pat. JP 2003252990* (2003).
3. Hirai, O.; Nishizawa, H.; Kawaguchi, H.; Fujimoto, K.; Okamura, A. *Jpn. Pat. JP 09302089* (1997).
4. Asao, K.; Morita, H.; Onishi, H.; Kimoto, M.; Yoshioka, Y.; Saito, H. *Jpn. Pat. JP 2000248063* (2000).
5. Ghatge, N. D.; Mulik, U. P. *J Polym Sci Part A: Polym Chem Ed* 1980, 18, 1905.
6. Kakimoto, M.; Akiyama, R.; Negi, Y. S.; Imai, Y. *J Polym Chem* 1988, 26, 99.
7. Fan, T.; Chen, J. D.; Huang, G. J. *J Funct Polym* 2007, 172, 19.
8. Hou, X.; Liu, B.; Deng, X. Zhang, B.; Chen, H.; Luo, R. *Anal Biochem* 2007, 368, 100.
9. Hong, J.; Hong, C.; Shim, S. *Colloids Surf* 2007, 302, 225.
10. Miwa, T.; Okabe, Y.; Ishida, M. *Polymer* 1997, 38, 4945.