Preparation and Functionalization of High Performance Polyimide Nanoparticles with Controllable Morphologies

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Polyimides are a class of representative high-performance polymers. At present, significant effort has been expended to improve their properties further by chemical modification and higher order structure control; our endeavors focused on the preparation and functionalization of high performance polyimide nanoparticles:

1: The crystallinity in polyimides provides advantages, so we first presented our work on morphological features formed during the thermal imidization procedure of aromatic polyimides derived from BTDA and m-PDA, in addition to zigzag Maltese crosses, the spherulites also showed concentric extinction rings, which are the characteristics of banded spherulites. The factors affecting the formation of banded spherulites were studied. The initial imidization conditions dramatically affected the formation of the banded spherulite morphology: slow heating (0.5C/min) or fast heating (20C/min) led to relatively small polyimide spherulites and less identifiable extinction rings. The relationship between the imidization procedure and the spherulite morphology formation was also studied. X-ray and FTIR together revealed that the novel banded crystalline morphology and structure were formed in the initial stage of the imidization process and were maintained during the following imidization processing at an elevated temperature.

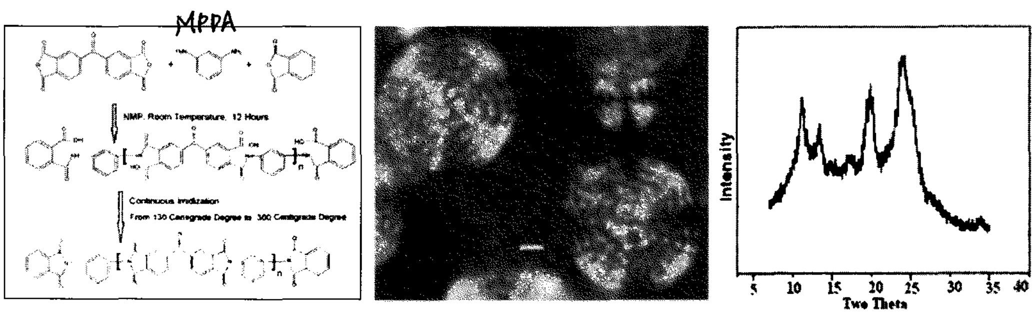

Fig. 1. Synthetic route of polyimides (left), banded spherulites (middle) and WAXD of the BTDA/m-PDA 0.95 polyimide at a heating rate of 5 C/min from 130 to 300 C (bar=10um).

2: We then reported a unique spontaneous self-assembly process that leads to the formation of polyimide nanoparticles with a novel dimpled-like morphology. To the best of our knowledge, this is the first example of macromolecular self-assembly where the rigid CPI serves as the only building block and the THF serves as the single solvent. The CPI can be readily dissolved in THF and results in a transparent solution. The solution gradually turned faint blue, as SEM clearly revealed, and the CPI self-assembled into uniform nanoparticles with a novel dimple-like morphology. The diameter of the resultant nanoparticles was dramatically affected by the solution concentration. The 0.1% CPI/THF solution resulted in nanoparticles with diameters around 300 nm. The 0.2% concentration resulted in nanoparticles with a diameter of about 450 nm, while the 0.5% concentration solution resulted in larger porous nanoparticles with a diameter of about 1 micrometer. Drawing a clear mechanism for the formation of hierarchical porous nanoparticles is still a challenge. On the basis of our experimental results, we propose a mechanism that involves a synergistic effect of the self-complementary hydrogen bonding between carboxyl end groups and the propensity of rigid polyimide chains to parallel pack as a result of the pi–pi stacking and/or aromatic donor–acceptor interaction.

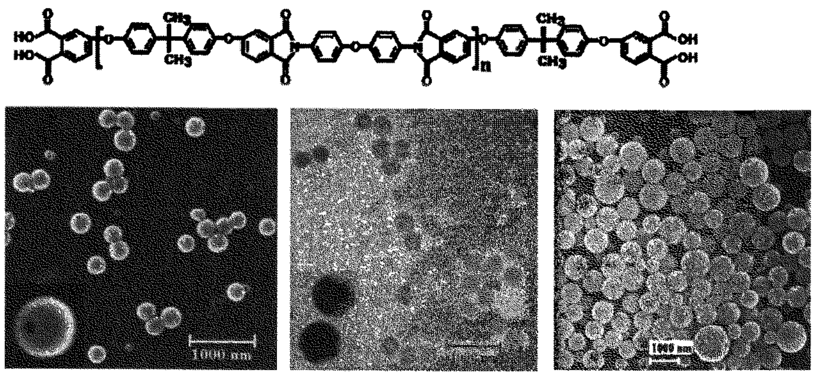

Fig. 2. SEM (left) and TEM (middle) images of nanoparticles with dimple-like morphology (0.1% CPI/THF solution), and SEM (right) image of nanoparticles (0.5% CPI/THF solution)

3: Finally we explored a facile and reproducible reprecipitation method for the preparation of high performance PI hollow spheres, and various novel morphologies, including bowle-like hollow sphere, deflated hollow sphere, dimple-like follow sphere and hollow spheres with complete shell can be easily manufactured by simply changing the PAA concentration. We further found that the added LiCl helps the formation of hollow spheres with closed shell. A mechanism of formation of these various morphologies was also proposed based on phase inversion principles. We believe this facile preparation process together with the existence of microporous shells will enable the potential uses of these novel materials in fields like supported nanocatalysis, controlled release and ultralow-dielectric-constant films.

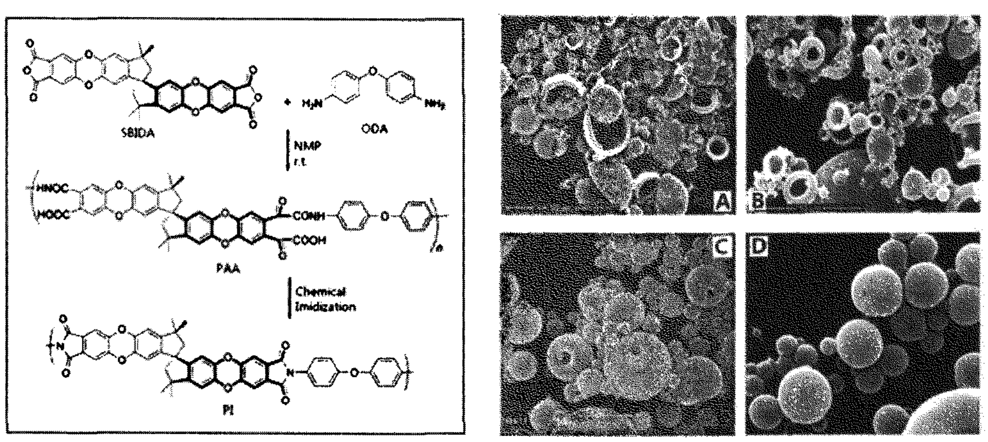

Fig. 3. SEM images of PAA hollow spheres with various morphologies: (A: 1 wt%, bowl-like, B: 2 wt%, deflated sphere, C: 5wt%, dimple-like, and D: 8wt%, complete hollow spheres)