

Preparation of A Novel Flower-Like Polyimide with Large Specific Surface Area

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Abstract: A novel flower-like polyimide was prepared via three-step and its properties and formation mechanism of flower-like structure were studied. It is demonstrated that the flower-like polyimide has large specific surface area (up to 2000m²/g). The formation of the flower-like structure is simultaneous with imidization and with the departure of small molecules.

Keywords: porous; polyimide; specific surface area

1. INTRODUCTION

Polyimide has been an important polymer material and a research hot-spot since the 1950s due to its unique structure and excellent properties [1]. It remains a promising material though the significant advances achieved in the field of material science and technology. Porous polyimide, which combines the excellent properties of polyimide and porous polymer, has have shown great application prospects in gas adsorption and separation[2], insulation and heat insulation[3], energy storage[4], catalyst carriers[5], porous carbon material precursor[6]and chemical sensing[7]. It has aroused widespread concern from researchers at home and abroad and has become a research hot-spot in recent years.

In this paper, a novel flower-like polyimide was prepared by a three-step method and its structure and properties were characterized. The formation mechanism of the flower-like structure was explored.

2. EXPERIMENTAL

2.1 Preparation of polyimide

Polyimide was prepared by a three-step method: esterification-salt forming reaction-thermal imidization process. Firstly, 1mmol tetracarboxydiphthalic ether dianhydride (ODPA, 99.5%) and excessive methanol were added to a flask equipped with condenser and reflux device, stirred for 4h at 75 °C until ODPA was dissolved into methanol and esterificated completely; thenequivalent hexamethylenediamine (DAH, analyze grade) was added into the system and white power was obtained after stirred for 1h and removed the excessive methanol and other molecules via spray drying; finally, the white powder was dissolved into glycol and heated to 165 °C and maintained for 4h with stirring, and yellow power was prepared after the solvent was removed and washed several times, followed by dried in vacuum oven for 12 h at 100 °C. Schematic of the preparation of polyimide by three-step method is showed by Figure 1.

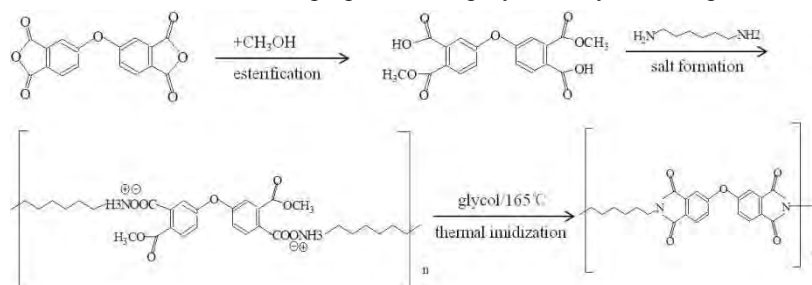


Figure 1. Schematic of the preparation of polyimide by three-step method.

2.2 Characterization of polyimide

Fourier transform infrared spectrum (FT-IR) was recorded by a JYH-74 NICOLET/10 infrared analyzer in ATR mode and the spectrum was recorded in 4000~500 cm⁻¹ region using 32 scans. Hydrogen nuclear

magnetic resonance spectroscopy($^1\text{H-NMR}$) were recorded with a Bruker AV 11-400 spectrometer linked to a computer running WIN-NMR software and experiments were carried out at 600 MHz in CF_3COOD with tetramethylsilane (TMS) as an internal reference at room temperature. Wide angle X-ray diffraction (WAXD) was performed on a Bruker D8 Discover at a speed of $1^\circ/\text{min}$, from $5^\circ\sim 36^\circ$ at room temperature. Samples for scanning electron microscopy (SEM) was first dispersed in ethanol, then dropped onto conductive adhesive and coated with a gold coating film about 100 \AA after ethanol volatilized, then carried on a Inspect EVO-18 JYJ-23. Differential scanning calorimetry (DSC) was conducted on a DSC 204 F1 in the temperature range of $40\sim 300^\circ\text{C}$ with a heating/cooling rate of $10^\circ\text{C}/\text{min}$ under nitrogen. The data (T_m , T_g) is the result of the first and second heating curve. Thermogravimetric analysis (TGA) was performed on using a JYH-85 TG analyzer, from 30 to 800°C with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. Specific surface area was detected by Micromeritics Tristar II 3020 V2.00 based on Brunauer-Emmett-Teller (BET) theory.

3. DISCUSSIONS AND RESULTS

3.1 Structure of polyimide

Firstly, chemical structure of resultant was verified by FT-IR (Figure 2a) and $^1\text{H-NMR}$ (Figure 2b).

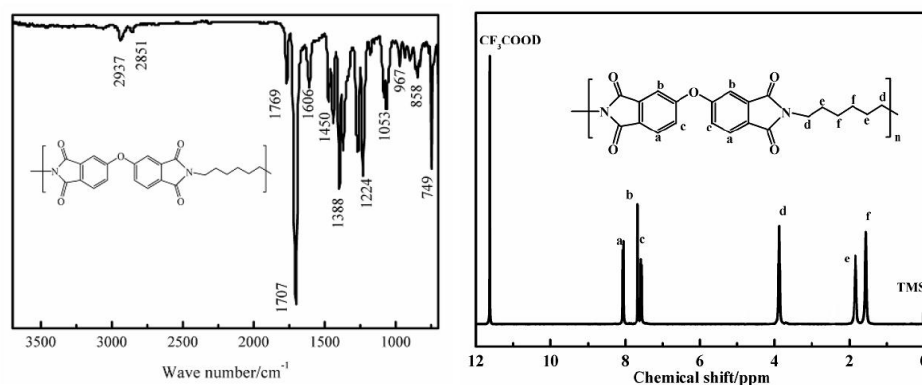


Figure 2. FT-IR and $^1\text{H-NMR}$ spectra of resultant prepared by three-step method.

Peak at 1707 cm^{-1} is attributed to the characteristic peak for $\text{C}=\text{O}$ of $-\text{N}-\text{C}=\text{O}$ structure and peaks at 1388 and 1769 cm^{-1} are ascribed to the stretching vibration of $-\text{C}-\text{N}-$ and $\text{C}=\text{O}$, respectively. 749 cm^{-1} is the characteristic absorption peak for aromatic imide group and 1606 and 1450 cm^{-1} belong to the stretching vibration of benzene skeleton. The peaks at 2937 and 2851 cm^{-1} are attributed to the stretching vibration of $-\text{CH}_2-$. Therefore, the resultant is polyimide. Besides, no peaks were observed at 1650 , 1550 and 3266 cm^{-1} , which is called amide II band, amide II band and stretching vibration of $\text{N}-\text{H}$. It suggested that the imidization is complete^[8]. The chemical shifts at $7\sim 8$ ppm are ascribed to the H atom of benzene ring (a,b,c), that at 3.8 ppm belongs to $-\text{CH}_2-$ near $\text{N}-\text{C}=\text{O}$ structure, and those at $1\sim 2$ ppm is associated with $-\text{CH}_2-$ structure far away. Besides, the area/height of the chemical shift peak is $1:1:1:2:2:2$, which is accordance with the designed structure. It suggested that the resultant prepared by three-step method is match with the designed structure and pure^[9].

Then the micro-structure of polyimide was studied by WAXD and SEM. As shown in Figure 3, the sharp diffraction peaks at $18^\circ\sim 25^\circ$ suggests that the segments and chains of polyimide arranged regularly and polyimide has high crystallinity^[10]. The peaks at different position are attributed to the different crystal faces and crystal orientations, which show anisotropy. The broader and lower peaks at 11.6° and 13.9° are ascribed to the amorphous structure of polyimide, which means polyimide is semi-crystal. The distance between different crystal faces calculated according Bragg formula, which is among $3.7\sim 4.8 \text{ nm}$, suggests that the

array points of the crystal surface are sparse but uniform. It is amazing that polyimide is micro-scale flower-like porous spheres, as a result of uniform arrangement by vast of nano-petal-like sheets. BET specific surface area of polymer is characterized (Figure 5), which comes out to be up to 2000 m²/g. Besides, the size of the holes are uniform, which among 2~4nm.

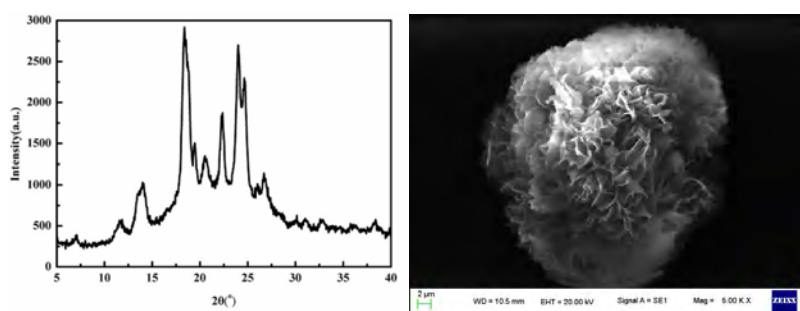


Figure 3. WAXD pattern of polyimide. Figure 4. SEM image of polyimide.

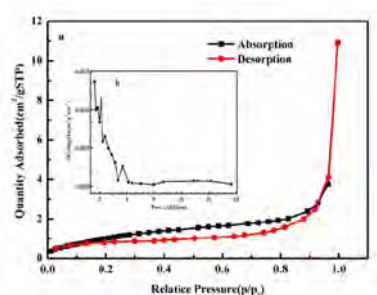


Figure 5. N₂ adsorption/desorption isotherms and pore size distribution of polyimide.

3.2 Thermal properties of polyimide

Thermal property is a key performance for polyimide. It can be seen from the DSC (Figure 6a) and TGA (Figure 6b) curves, polyimide show excellent thermal properties. The glass transition temperature (T_g) and melt temperature (T_m) of polyimide is 126 °C and 252 °C, respectively, which is slightly lower than aromatic polyimide because of the introduction of aliphatic chain. The initial degradation (T_{5%}) and maximum degradation temperature (T_{max}) of polyimide is up to 464 °C and 504 °C, respectively, though a slight weight loss is observed among 100~200 °C, which is attributed to the removal of the remained solvents.

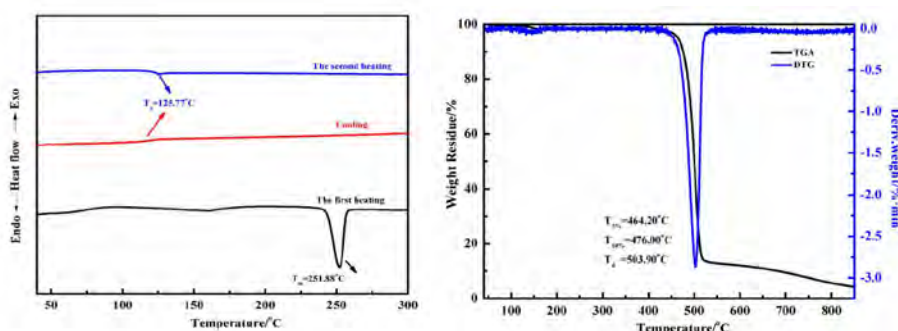


Figure 6. DSC and TGA curves of polyimide.

It is interesting that no crystallization is observed in the cooling curve, neither melting in the second heating curve, which can be ascribed to the tough crystal condition the polyimide needs. It can gradually seed out in the solvent and arranged in order, while remains amorphous in bulk.

3.3 Formation mechanism of flower-like structure

In order to explore the formation mechanism of the amazing flower-like structure, which led to the huge

specific surface area of polyimide, samples from different reaction times were investigated.

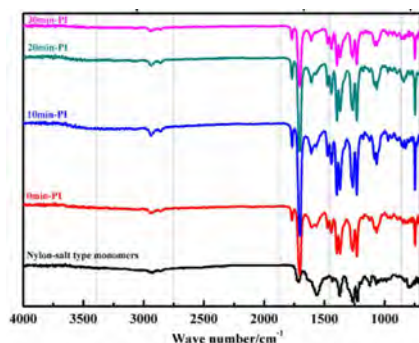


Figure 7. FT-IR spectra of samples from different reaction time.

It can be seen from the FT-IR spectra that the peak at 1559 cm^{-1} , which was attributed to amide II band (the deformation vibration of N-H in $-\text{CONH}-$ structure), reduced gradually and disappeared when reacted for 30 min. While characteristic peaks for C=O (1770 cm^{-1}) and C-N ($1380, 1100$ and 749 cm^{-1}) emerged and remained. Therefore, the nylon-type monomer imidization completely after reacted for 30 min. Morphology of samples was also investigated, as shown in Figure 8. The aggregate collected is solid spheres when newly emerges. Holes gradually appear after heated for 10 min and flower-like structure comprised of curly petal-like sheets is formed after 20 min. Then the micro-structure of polyimide become stable when reacted for 30min, which is accordance with the results of FT-IR.

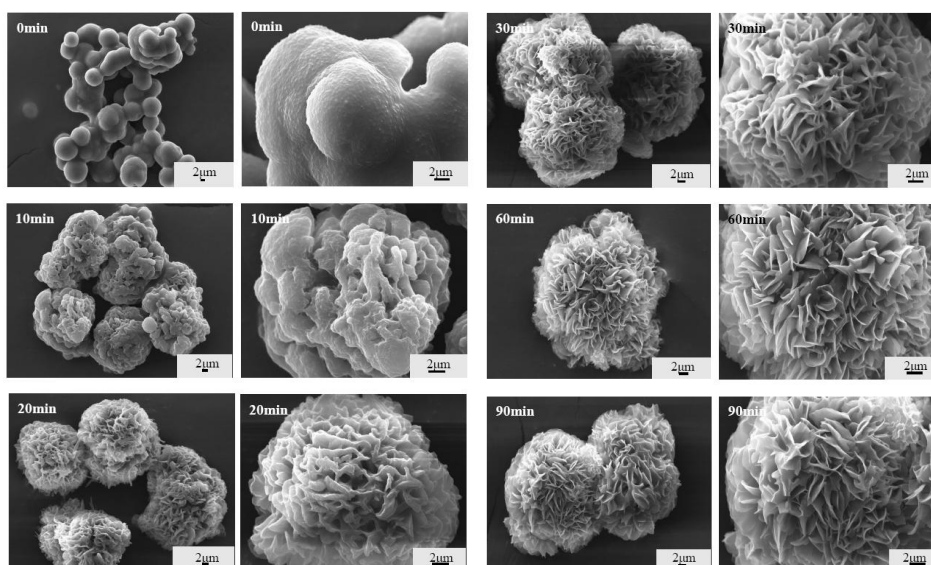


Figure 8. SEM images of samples from different reaction time.

According to the TGA curve of nylon-type monomer (Figure 9), there are three weight loss stages: the first stage (below 120°C , 6.71% weight loss) and second stage (among $120\sim 180^{\circ}\text{C}$, 11.6%) are mainly attributed to the removal of H_2O and CH_3OH produced in imidization process, and the third one (among $450\sim 800^{\circ}\text{C}$, 72.7%) is ascribed to the degradation of polyimide. So the flower-like structure is formed in three stages: firstly, when the nylon-type monomer solution was heated, imidization happened and polyimide seeded out and aggregated gradually to form solid sphere with CH_3OH and H_2O molecules inside when the temperature is below 120°C ; as the temperature became higher, holes emerged as a result of the removal of small molecules; when the temperature reached 165°C , polyimide chain self-assembled on the surface of the

seeds due to Π - Π staking, which brought out numerous holes comprised by curly petal-like sheets, and formed the flower-like structure. What was more, the petal became more flat and the flower-like structure become more stable as the imidization becoming more complete. Therefore, the formation of the flower-like structure is simultaneous with imidization.

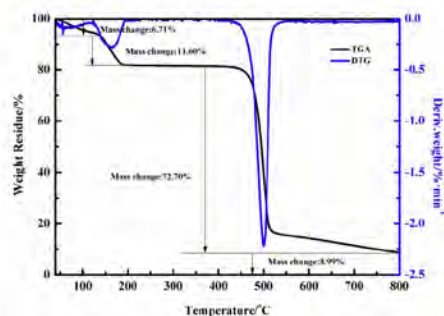


Figure.9. TGA curve of nylon-type monomer.

4. CONCLUSIONS

In conclusion, a novel flower-like porous polyimide with large specific surface area was prepared via a three-step method. Polyimide obtained is a flexible, heat resistant and processable porous material, which has broad application prospect. The formation of the flower-like structure is simultaneous with imidization and with small molecules produced as porogen. Besides, the method is easy, environmental-friendly, and with low cost, which can be generalized to prepare porous polymer materials.

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