

Self-assembly of rod-coil multiblock polyimides into flower-like microparticles through precipitation polymerization

(Dept. of Mat. Sci. and Eng. Tokyo Tech.¹)

Yuqian Chen¹, Kan Hatakeyama¹, Yuta Nabae¹, Teruaki Hayakawa¹

Abstract

This study aims to simultaneously control the shape morphology of particles composed by rod-coil multiblock polyimides at the micro-scale and the higher-ordered structure of the particle at the nanoscale through precipitation polymerization. Diamines within different alkyl chain lengths were successfully prepared. Spherical particles and flower-like particles (FLPs) were successfully prepared in the mixed solvent of cyclohexanone/acetone. Hansen solubility parameter was calculated to quantitatively evaluate the interaction between the polymers and the solvents. Based on the small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) profiles and POM images of the FLPs, it is considered the flower-like morphology originated from the microcrystalline structure of the folded and stacked alignment of poly(amic acid) molecules. The solubility was decisive to the crystallization speed and its growing method, which resulted in the variation in FLP size. The flower-like structure was well maintained after the thermal imidization and carbonization, which shows its possibility to serve as catalyst support material in proton exchange membrane fuel cells (PEMFCs) to enhance the catalyst efficiency.

Introduction

Many efforts have been made to enhance the electrocatalyst efficiency on the cathode side of the proton exchange membrane fuel cells (PEMFCs), given the use of scarce Pt catalyst, which is now the major hindrance to the globalization of PEMFCs.^[1] One of the strategies is to use mesoporous carbon as the catalyst support material. Previously, polyimide precursor and mesoporous carbon were fabricated using a self-assembled block copolymer as the template.^[2] Polyimide particles were successfully fabricated through precipitation polymerization as the precursor of carbon particles.^[3] Herein, the research interest of this study is to simultaneously control the shape morphology of the carbon into particles and self-assembled higher-ordered structure into mesopores from polyimide precursors prepared through precipitation polymerization.

Recently, polymeric flower-like particles (FLPs) have been reported as examples of particles self-assembling into higher-ordered structures. For example, polyimides were reported to form FLPs through the solvothermal method.^[4] Other research has also shown the formation of FLPs was related to the crystalline structure of the polymer.^[5-7]

Block copolymers (BCPs) are composed of two or more chemically dissimilar polymer blocks joined by covalent bonds. In the simplest case of coil-coil diblock copolymers, the thermodynamically immiscible blocks enable BCPs to spontaneously form microphase-separated structures. Compared to coil-coil BCPs, the study on rod block containing BCPs is still in the seminal stage. Most of the rod polymers can only be prepared through step-growth polymerization, which leads to broad molecular weight distribution. The combination of rod polymers and coil polymers results in unique self-assembly behavior that differs remarkably from that of traditional coil-coil BCPs due to the interplay between the rod and coil components. The anisotropic nature of the rod-like chains also leads to anisotropic interactions between the blocks, resulting in the potential for liquid crystalline ordering.^[8]

In this work, diamines composed of rod and coil segments, bis(4-aminophenyl) 4,4'-(dodecane-1,12-diylbis(oxy))dibenzoate (DA-6) and bis(4-aminophenyl) 4,4'-(dodecane-1,12-diylbis(oxy))dibenzoate (DA-12), were specially designed and synthesized to conduct precipitation polymerization with pyromellitic dianhydride (PMDA) to produce rod-coil

multiblock poly(amic acid) (PAA) particles. After thermal imidization and carbonization, the aliphatic segments are decomposed, forming mesoporous carbon particles.

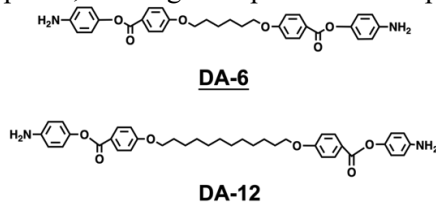
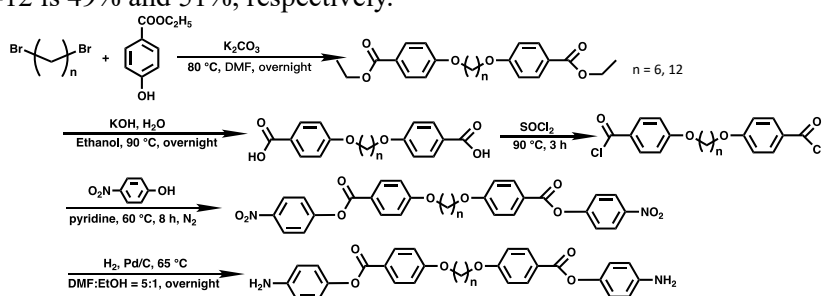


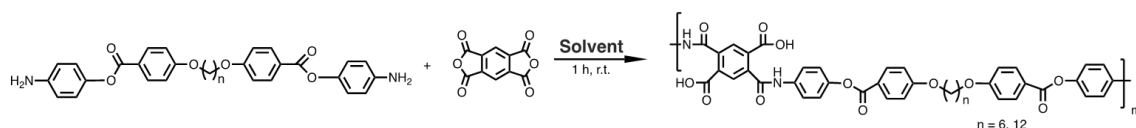
Fig. 1 Chemical structures of diamines synthesized in this research.

Experimental

DA-6 and DA-12 were synthesized through 5 steps as shown in scheme 1. The overall yield of DA-6 and DA-12 is 49% and 51%, respectively.



Scheme 1 Synthesis of DA-6 and DA-12.



Scheme 2 Precipitation polymerization of DA-6/PMMA and DA-12/PMMA.

The typical process of precipitation polymerization of DA-6 and DA-12 was conducted as follows: 0.25 mmol of diamine and PMDA were dissolved in the mixed solvent respectively. Once the monomer was well dissolved and dispersed, the diamine solution was added to the PMDA solution, and the mixture was vigorously stirred at room temperature for 1 h under an N₂ atmosphere. The mixed solvents were cyclohexanone/acetone (cyc/ace), cyclohexanone/toluene (cyc/tol), acetophenone/toluene (ap/tol), acetophenone/acetone (ap/ace). The mixed solvent volume ratio was varied while the total volume was kept at 100 mL.

The precipitation was collected through centrifugal separation and repeatedly washed 3 times. The powder was dried at 40 °C under a vacuum overnight to get the pale yellow poly(amic acid) particles. By heating the poly(amic acid) particles at 240 °C for 3 h under vacuum, the light brown powder of polyimide particles was obtained. The polyimide particles were carbonized in N₂ with a ramping rate of 1 °C/min to 900 °C.

Results and discussion

DA-6/PMMA PAA particles prepared in the mixed solvent of cyclohexanone/acetone exhibited flower-like morphology (Fig. 2 (a-d)), which was different from those prepared from cyclohexanone/toluene (Fig. 2 (k-n)). The flower-like morphology was well-maintained after the thermal imidization and carbonization. The cross-section of the FLPs verified the hollow structure inside the PI particles and the carbon particles (Fig. 2 (g-j)). On the other hand, DA-12/PMMA PAA particles in general showed less well-confined particle morphology (Fig. 2 (o), (p)).

The WAXD and POM showed microcrystalline structure existed in both DA-6/PMMA and DA-12/PMMA PAA particles (Fig. 2 (b)). To further figure out the reason for the morphology difference between DA-6/PMMA and DA-12/PMMA, the Hansen solubility parameter (HSP) was

calculated (Table 1). The HSP distance of DA-12/PMDA was larger than DA-6/PMDA, indicating the better affinity to the mixed solvent of cyclohexanone/acetone, which may result in its difficulty in forming the self-confined particle morphology due to the longer alkyl chain.

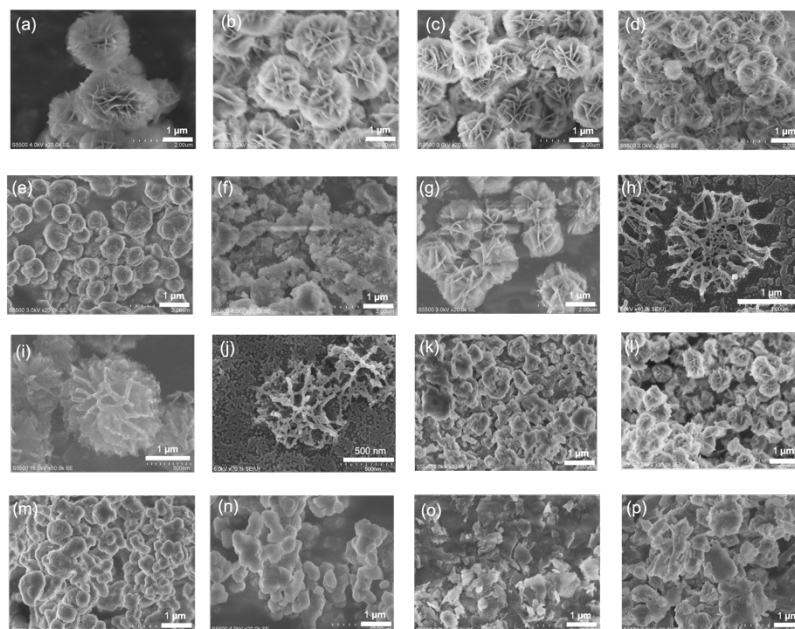


Fig. 2 FE-SEM images of DA-6/PMDA PAA particles prepared in cyc/ace = 2:8 (a), 3:7 (b), 4:6 (c), 5:5 (d), 6:4 (e), 7:3 (f); FE-SEM image and its cross-section image of DA-6/PMDA PI particles prepared in cyc/ace = 2:8 (g, h); FE-SEM image and its cross-section image of DA-6/PMDA carbon particles prepared in cyc/ace = 2:8 (i, j); FE-SEM images of DA-6/PMDA PAA particles prepared in cyc/tol = 3:7 (k), 5:5 (l), 7:3 (m), 8:2 (n); Representative of DA-12/PMDA PAA particles prepared in ap/tol = 3:7 (o), and 5:5 (p).

The flower-like DA-6/PMDA particles showed unique SAXS patterns compared to DA-6/PMDA bulk film at $d \approx 6.5$ nm (Fig. 3 (a)). The WAXD of flower-like DA-6/PMDA particles showed sharp peaks around $2\theta \sim 20^\circ$ (Fig. 3 (b)), indicating the interchain distance of the stacking aromatic blocks was 0.44 nm. Based on these experimental facts, the formation mechanism of the flower-like particles in this research is proposed as the rod-coil multiblock polymer chains are folded and stacked to form the petal layer of the flower-like structure (Fig. 3 (c)).

Flower-like particle size exhibited a relationship with the solubility of mixed solvent (Fig. 2 (a)~(d)). When the mixed solvent system of cyclohexanone showed lower solubility with a larger volume fraction of acetone, the diffusion of polymer chains was hindered, resulting in a faster crystalline formation. The polymer chains tended to be randomly attached to the existing lamella, eventually forming particles with larger particle sizes. On the contrary, when the system showed higher solubility, the diffusion of polymer chains was promoted to form more compressed layer-layer lamella and smaller particles.

Conclusion

Rod-coil multiblock polyimide particles were successfully prepared through precipitation polymerization. DA-6/PMDA FLPs were produced in the mixed solvent of cyclohexanone/acetone. Flower-like morphology was related to the rapid formation of microcrystalline DA-6/PMDA in the solvent with lower solubility. FLPs showed excellent thermal stability and maintained their flower-like morphology after carbonization.

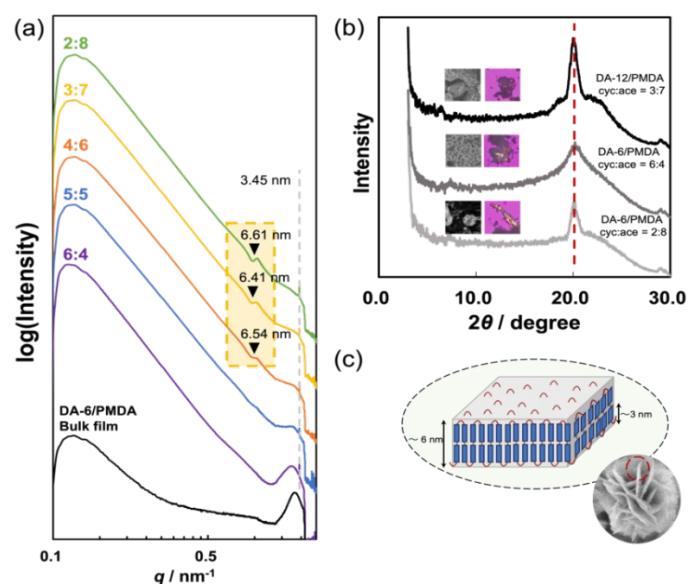


Fig. 3 (a) SAXS profile of DA-6/PMDA PAA particles and DA-6/PMDA bulk film; (b) Comparison of WAXD profile and POM images@r.t. of irregular, spherical, and flower-like particles; (c) Proposed formation mechanism of FLPs in this research.

Table 1 Hansen solubility parameter of DA-6/PMDA and DA-12/PMDA in cyc/ace.

Volume ratio (cyc/ace)	δ_d	δ_p	δ_h	HSP Distance	
				DA-6/PMDA	DA-12/PMDA
7:3	17.1	9	5.7	15.39	13.11
6:4	16.9	9.2	5.9	15.75	13.49
5:5	16.6	9.2	5.9	16.33	14.06
4:6	16.4	9.6	6.2	16.71	14.45
3:7	16.2	9.8	6.4	17.09	14.85
2:8	16.0	10.0	6.6	17.48	15.24

Acknowledgment

This study was financially supported by JSPS KAKENHI (21K04828). Scanning electron microscopy was performed under the assistance of Ryohei Kikuchi (OFC, Tokyo Tech.) and a MEXT project (JPMXS0420900521). SAXS measurements were carried out at BL40BII in SPring-8 under the assistance of Prof. Tomoyasu Hirai (Osaka Institute of Technology) and Dr. Noboru Ohta (JASRI).

References

- [1] Suter, T. A. M. et al. *Adv. Energy Mater.* **2021**, 11 (37), 2101025.
- [2] Gao, L. et al. *Polym. J.* **2018**, 50 (5), 389–396.
- [3] Hori, K. et al. *J. Photopolym. Sci. Technol.* **2020**, 33 (3), 327–332.
- [4] Wang, Y. et al. *J. Energy Storage.* **2022**, 55 (PA), 105390.
- [5] Zhang, K. et al. *ACS Macro Lett.* **2015**, 4 (2), 214–219.
- [6] Chen, S. et al. *J. Am. Chem. Soc.* **2018**, 140 (32), 10297–10304.
- [7] Liu, X. et al. *Angew. Chemie - Int. Ed.* **2021**, 60 (52), 27026–27030.
- [8] Kallitsis, J. K. et al. *Elsevier: Amsterdam.* **2012**, pp 725–773.