Title of Thesis

Study on Morphology Control of Aromatic Polyimide Particles by Using Environmentally Benign Solvent

SEPTEMBER 2015

DAISAKU SHOJO

The Graduate School of Environmental and Life Science

(Doctor Course)

OKAYAMA UNIVERSITY

CONTENTS

INTRODUCTION

Aromatic polyimides have been well known as useful high-performance materials because of their outstanding properties such as thermal stability, mechanical property, chemical resistance, radiation resistance and so on. [1-6] Therefore, aromatic polyimides represented by KAPTON and UPILEX have been widely used in various industrial fields like aerospace materials, membranes, electronic devices and so on. [7-11] These properties are caused by their rigid structures consisted of aromatic rings and cyclic imide linkages, which give strong π–π interactions. Among them, poly(*p*-phenylene pyromelliteimide) (PPPI) are expected to possess the highest performance in all organic polymers besides carbon fibers because of its rigid and straight structure. The theoretical modulus of PPPI predicted from the chemical structure is over 500GPa. [12] However, it is difficult to fabricate these aromatic polyimides to useful materials due to their infusibility and insolubility caused by their rigid structures. Therefore, they are usually fabricated by the two-step method *via* the formation of corresponding poly(amic acid)s as soluble precursor. Tetracarboxylic dianhydrides and diamines are reacted in a polar aprotic solvent to produce the poly(amic acid)s, and then the poly(amic acid)s are formed into fibers and films. Finally, they are chemically or thermally imidized, resulting in the formation of the polyimide fibers and films.

In these days, morphology control of polymers to yield particles and fillers has been paid attention from the view point of their unique properties. Particles of common polymers have been prepared, which are hollow sphere, hemisphere, porous particles, ribbons, plates and so on, and they are used in various applications, biomedical, nano- and meso-scaled reaction vessels, optical material, surface modifier and so on. [13-17] They have been mainly prepared by the dispersion polymerization such as the emulsion polymerization and the suspension polymerization.[18-19] In suspension polymerization, hollow particles whose size was 150-700 nm in diameter were prepared by using SiO_2 particles having narrow diameter distribution as core materials and subsequent etching them after polymerization. [14] Hemispherical polystyrene (PS)

particles were also prepared by microsuspension polymerization of styrene in water and hexadecane (HD) dispersion, and followed by removal of HD.[16] Beside them, re-precipitation method and precipitation polymerization method are also widely used to prepare various polymer particles and fillers including aromatic polyimides.[20-23] In the former method, polymer particles were prepared as precipitates from polymer solution by adding poor solvent for them. In the latter method, polymerization proceeded in homogeneous solution in which monomers and initiators were completely soluble, and then polymer particles were obtained as precipitates because obtained polymers were insoluble in the solution. In recent years, self-assembling method has been developed and it has enabled us to control not only the morphology of polymers but also their higher-order structures including the crystal structure, direction of molecular orientation and so on.[24-29] These polymers are expected to possess outstanding properties such as high thermal conductivity and second order non-linear optical properties owing to their regular crystal structure and hyperpolarization generated along the molecular chains.[30, 31] Although it is of great importance for high performance polymers such as aromatic polyimides to control the higher-order structures in order to obtain the essential properties predicted by their chemical structures, the control of them is very difficult due to the intractability described above. The research group of Okayama University has been studying the morphology control of wholly aromatic polymers including aromatic polyimides by reaction-induced phase separation of oligomer during solution polymerization, and whiskers of poly(*p*-oxybenzoyl) (POB), lozenge crystals and micro-flowers of PPPI, and nano-scaled ribbons-like crystals of poly(4-phthalimide) (PPI) were successfully prepared by polymerization in non-polar and high boiling temperature solvent such as liquid paraffin or a mixture of isomers of dibenzyltoluene (DBT).[32-37] These morphologies were shown in Figure 1. The molecular chains were aligned along the long axis of them, and they possessed high crystallinity. Especially, the POB whiskers exhibited single-crystal nature. Thus, this method is unique procedure which enables us to control not only the morphology but also the higher-order

structure of the intractable polymers.

Within the past decades, green chemistry has been getting a lot of attention and has developed in various scientific fields such as synthesis of organic chemistry, polymer synthesis, process engineering and so on. [38-42] Among the twelve principles of green chemistry, [43] utilization of “safer solvents” is a very important part in chemical industry, because large amounts of solvent were used to produce industrial products. Therefore, the use of environmentally benign solvent has been strongly required. Then considerable efforts have been devoted to develop alternative solvent for chemical synthesis, and various solvents such as supercritical carbon dioxide, ionic liquids, water and alcohol have been studied as “green solvent”. [44-46] There are some debates about ”what a green solvent is”. However, water and alcohol can be considered as green solvents, because water is not only nontoxic but also nonflammable, and alcohol was also very low toxic and environmentally benign from the view point of life-cycle assessment. [42-46] Synthesis of organic chemistry in water and alcohol has therefore become of great interest and synthesis of polymers has also been investigated. For example, isopropyl alcohol was examined as a green solvent for the synthesis of silicone-urea copolymers. [47] However, polycondensation reactions to synthesize polyesters are determined by the equilibriums, and therefore it is difficult to synthesize them in water but for the polymerization using lipase-catalyzed system. [48] In recent years, dehydration reaction in water with surfactant-type Bronsted acid was reported and this methodology was applied for polyester synthesis in water. [49, 50] In this previous report, polycondensation reaction of sebacic acid and dodecanediol was examined with *p*-dodecylbenzenesulfonic acid (DBSA) as surfactant-type Bronsted acid. This reaction could be understood as follows; at first micelles of monomers were formed in water solution with the aid of DBSA as a surfactant, and then condensation reaction was activated by the sulfonate group in DBSA to afford polyesters in the micelle with eliminating water. On the other hand, aromatic polyimides and aromatic poly(amide-imide)s were synthesized in water without using such a specialized surfactant. [51-53] Specifically, high

molecular weight Ultem-type polyimide was successfully synthesized by hydrothermal reaction of equimolar 2,2-bis[4-(dicarboxyphenoxy)phenyl] propanes and 1,3-phenylene diamines at 180^{o}C for 2h. The mechanism of the synthesis of polyimides in water was discussed in previous study. [54] Insoluble components such as nylon type salt compounds and oligomers were formed in water and then polymerization proceeded in them as solid-state polymerization. These results imply that the key point of the polymer synthesis in water is a separation of the reaction phase from water solution. As described above, various polymer particles and fillers were prepared by mainly utilization of phase separation of polymers. Therefore it might be possible to control the morphology of aromatic polyimide particles by using phase separation phenomena in water. If the morphology of aromatic polyimide particles were controlled by using environmentally benign solvents such as water and alcohol, it enables us to prepare the high performance fillers at environmentally benign and safer process.

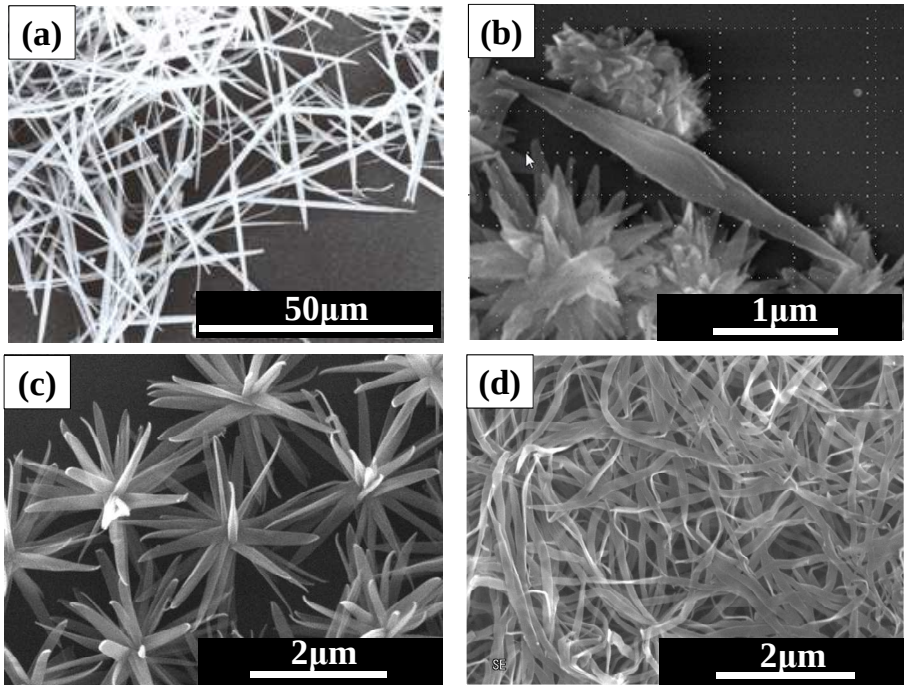


Figure 1 SEM images of (a) POB whiskers, (b), (c) lozenge crystals and micro-flower crystals of PPPI and (d) PPI nano-ribbons.

AIM AND STRATEGY OF THIS THESIS

On the basis of the above description, the aim of this thesis is an establishment of the morphology control method for aromatic polyimide particles by using environmentally benign solvents like water and alcohol. In order to accomplish this thesis, I focused on two methods to prepare aromatic polyimide particles. One is the combination of the preparation of salt monomers derived from aromatic tetracarboxylic acid and aromatic diamine in water and solid-state polymerization (SSP) of them. Another is that using reaction-induced phase separation of oligomers during aqueous solution polymerization.

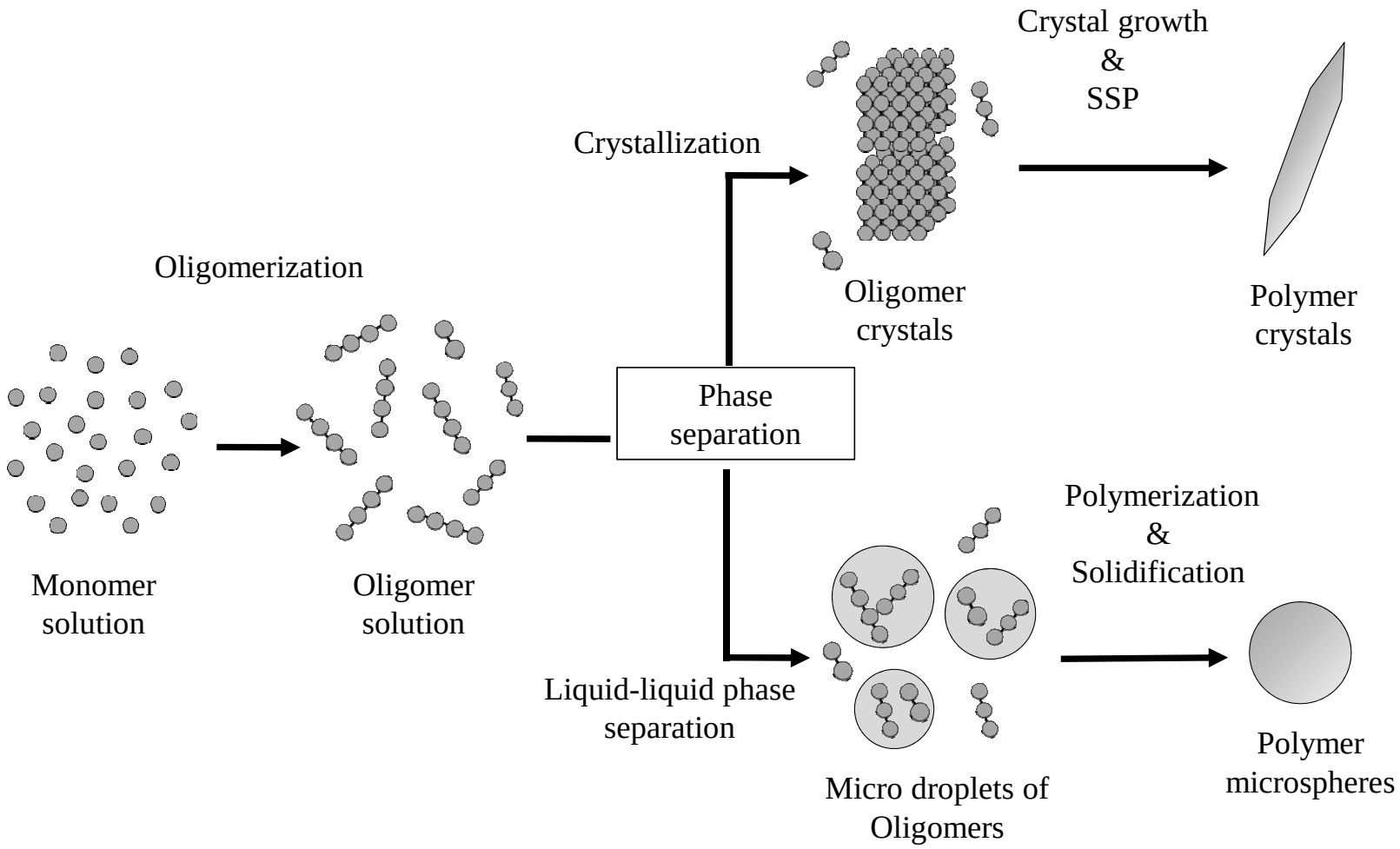
SSP of salt monomers has been previously studied to prepare polyimides. [55-60] In these studies, salt monomers derived from aromatic tetracalboxylic acids and aromatic or aliphatic diamines were prepared by precipitation method from various solvents, and high molecular weight aromatic polyimides were synthesized by subsequent SSP of them. Therefore, if the morphology of salt monomers can be controlled by tuning the precipitation conditions and their morphology can be maintained during SSP, this method becomes facile method to prepare polyimide fillers.

Next, I explain about the principle of the reaction-induced phase separation of oligomers in order to understand basic concept for morphology control of aromatic polyimides by this method. Schematic drawing of reaction-induced phase-separation of oligomers during solution polymerization is illustrated in Scheme 1. In order to induce the phase separation of oligomers, the solvents which are miscible for monomers and immiscible for oligomers are required. The physical properties of the oligomers such as solubility change drastically with increasing molecular weight of them, resulting in causing phase-separation through super-saturated state. In the case of aromatic imide-oligomers, the phase separation behavior of them during aqueous solution polymerization is considered to be upper critical solution temperature (UCST) type as

depicted in Figure 2, because the physical interactions between the oligomers and water molecules such as hydrogen bond and hydrophilic interaction are weak due to their chemical structure. This *C*-*T* phase diagram is the analogue *C*-*T* phase diagram on partially miscible polymer-solvent system. [61, 62] There are two modes for the phase separation of oligomers, of which one is the crystallization and another is the liquid-liquid phase separation. If the super-saturated oligomers phase-separated across the freezing point curve, oligomer crystals were obtained as precipitates. Then subsequent crystal growth occurred by supply of oligomer from the solution and SSP occurred simultaneously, and finally the polymer crystals are formed such as whisker. On the other hand, if they are phase-separated *via* liquid-liquid phase separation, microdroplets of dense phase are formed in the dilute phase. In the microdroplets, the further polymerization proceeds efficiently due to the higher concentration of oligomers, and then oligomers are crystallized in them. Consequently, the surface of the microdroplets is stabilized by the solidification and microspheres are finally obtained. Thus, key points of this method are the introduction of phase separation of oligomers and subsequent SSP. As described before, polyimide was prepared in water by separation of the reaction phase from water solution. Therefore, morphology control of aromatic polyimide particles in water might be possible by means of reaction-induced phase separation during aqueous solution polymerization as shown in Scheme 2.

This thesis consists of three chapters. In Chapter 1, the previous studies about the morphology control of aromatic polyimide particles were reviewed in order to find out possible methods of morphology control of them in environmentally benign solvents and to clarify the usefulness and the importance of the ideas in this doctoral dissertation. Chapter 2 is described the morphology control of four kinds of aromatic polyimide, which are PPPI, poly(4,4’-oxydiphenylene pyromellitimid), poly(*p*-phenylenebiphenyl tetracarboximide) and poly(4,4’-oxydiphenylenebiphenyltetracarboximide), by means

of SSP of crystals of the nylon-type salt monomers derived from aromatic tetracarboxylic acids and aromatic diamines. In this chapter, influence of preparation conditions of salt monomers on the morphology and higher-ordered structure of obtained PPPI crystals were also discussed. In Chapter 3, the reaction-induced phase-separation during aqueous solution polymerization of aromatic polyimides represented by PPPI was examined.



Scheme 1 Schematic drawing of reaction-induced phase separation of oligomers during solution polymerization.

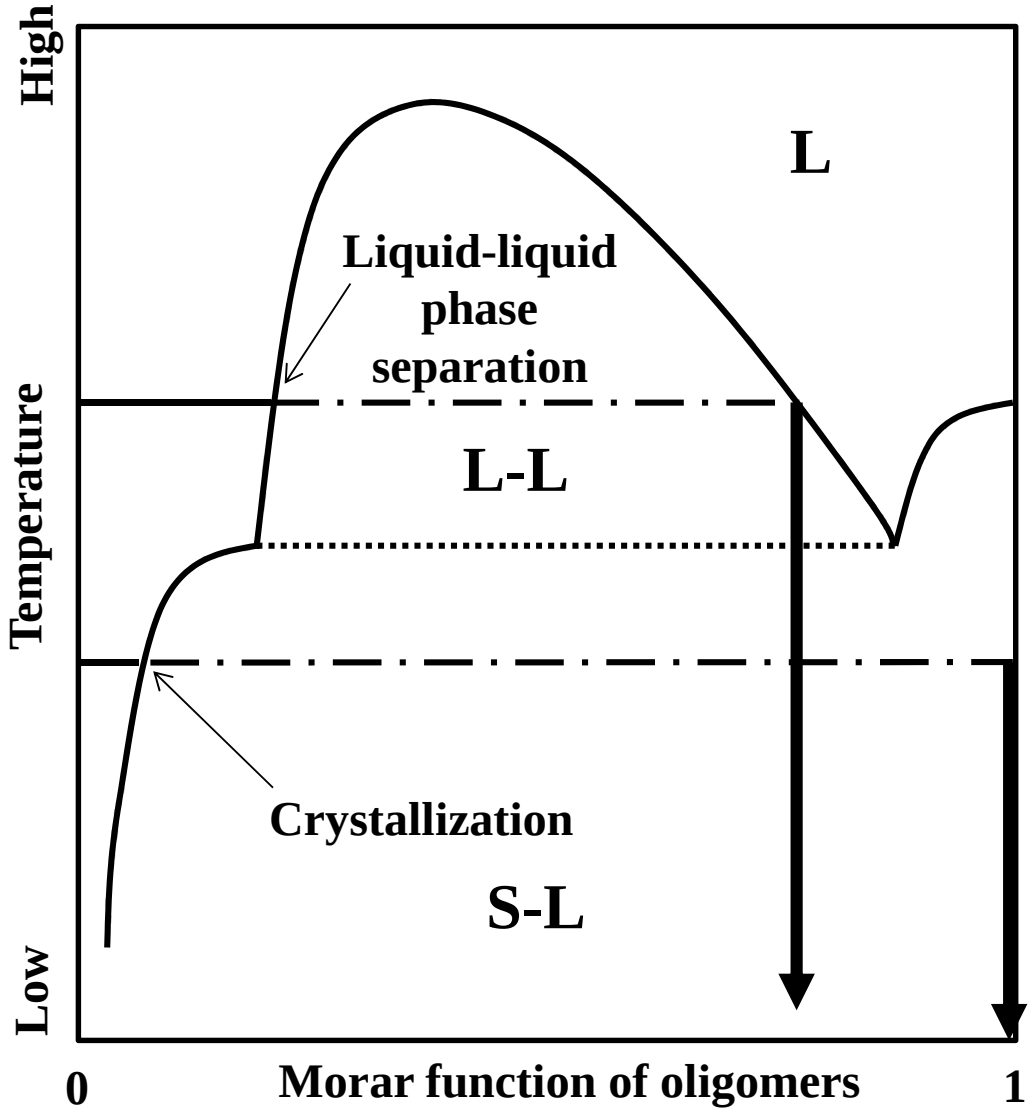
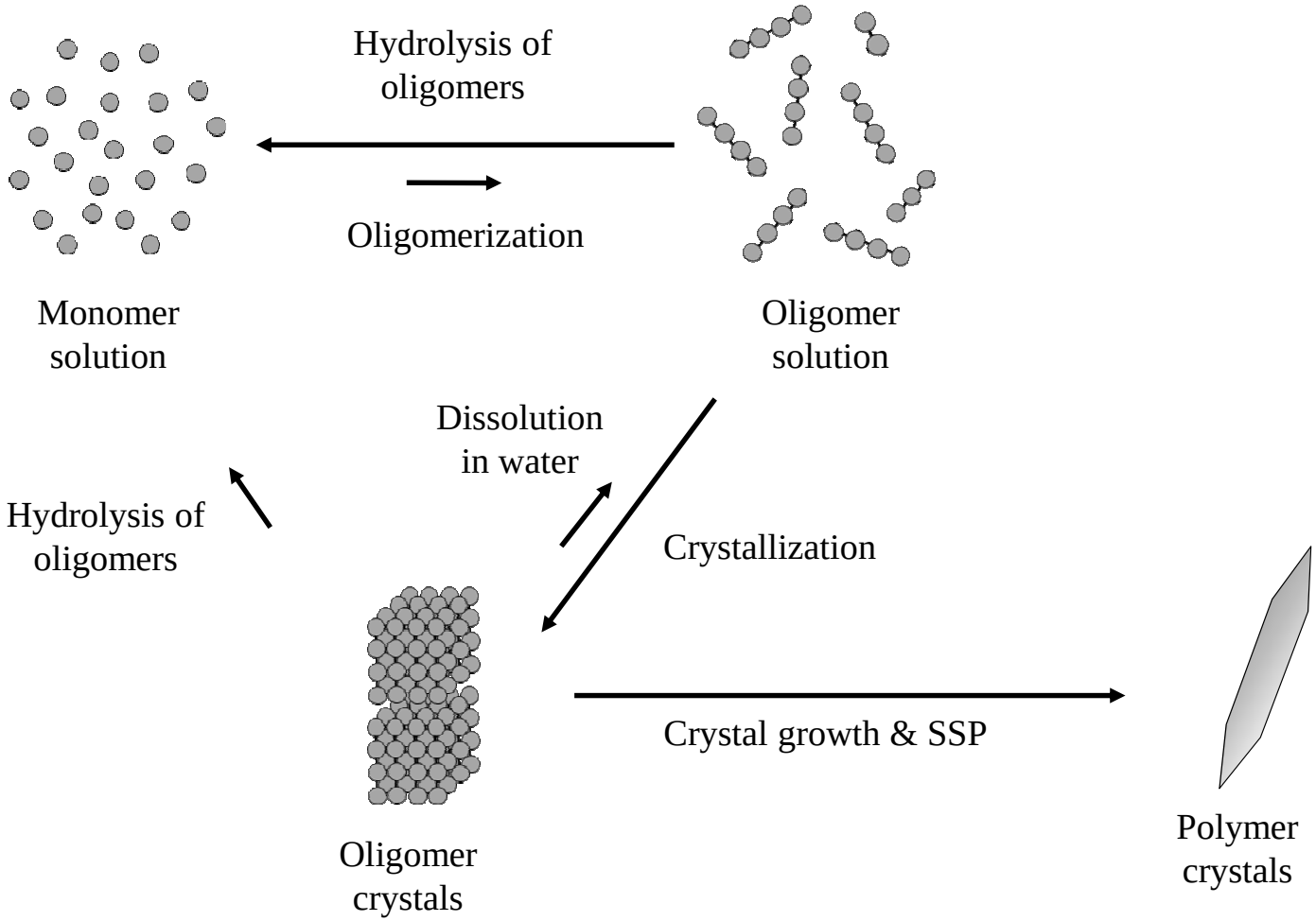


Figure 2 Schematic *C-T* phase diagram for partially miscible oligomers and solvent system. (L: miscible liquid phase, L-L: two immiscible liquid phases, S-L: Liquid-solid phase)



Scheme 2 Schematic drawing of concept for synthesis of aromatic polyimide by means of reaction-induced crystallization during polymerization in aqueous solution.

References

1. C. E. Stroog, *Polyimides: Fundamentals and Applications*, M. K. Ghosh, K. L. Mittal, eds., pp.1-6, Marcel Dekker, New York, 1996
2. K. L.Mittal, *Polyimides: Synthesis, Characterization, and Application, Vol. 1*, Plenum Press, New York, 1984
3. M. I. Bessonov, M. M. Koton, V. V. Kudryavtsev, L. A. Laius, *Polyimides: Thermally Stable Polymers*, New York: Consultants Bureau; 1987.
4. D. Wilson, H. D. Stenzenberger, P. M. Hergenrother, *Polyimides*, New York: Blackie; 1990.
5. T. Takekoshi, *Polyimides*, D. Wilson, H. D. Stenzenberger, P. M. Hergenrother, eds., pp.38-57, Blakie, Glasgow, 1990
6. W. Volksen, *Adv. Polym. Sci.*, **117**, 111, 1994
7. R. Yokota, R. Horiuchi, *J. Polym. Sci., Part C; Polym. Lett.*, **26**, 215, 1988
8. K. Vanhercka, G. Koeckelberghsb, I. F. J. Vankelecoma, *Prog. Polym. Sci*., **38**, 874, 2013
9. S. Numata, S. Oohara, K. Fujisaki, J. Imaizumi, N. Kinjo, *J. Appl. Polym. Sci.*, **31**, 101, 1986
10. N. Sato, S. Shigematsu, H. Morimura, M. Yano, K. Kudou, T. Kamei, K. Machida, *IEEE Trans.*, **52**, 5, 1026, 2005
11. J. M. Zara, S. M. Smith, *IEEE Trans.*, **49**, 7, 947, 2002
12. K. Tashiro, M. Kobayashi, *Sen'i Gakkaishi*, **43**, 78, 1987
13. J. Ugelstad, H. R. Mfutakamba, P. C. Mork, T. Ellingsen, A. Berge, R. Schmid, L. Holm, A. Jorgedal, F. K. Hansen, K. Nustad, *J. Polym. Sci.: Polym. Symp.*, **72**, 225, 1985
14. X. Xu, S. A. Asher, *J. Am. Chem. Soc.*, **126**, 7940, 2004
15. T. Takami, Y. Murakami, *Langmuir*, **30**, 3329, 2014
16. T. Yamagami, T. Tanaka, T. Suzuki, M. Okubo, *Colloid Polym. Sci.*, **291**, 71, 2013
17. M. O. Mizrahi, S. Margel, *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 4612, 2007
18. P. A. Lovell, M. S. E. Aasser, *Emulsion Polymerization and Emulsion Polymers*, Wiley, New York, 1997

19. R. Arschady, *Polym. Eng. Sci.*, **33**, 865, 1993

20. J. Liu, Y. Yan, Z. Chen, Y. Gu, X. Liu, *Chem. Lett.*, **39**, 1194, 2010

21. G. Zhao, T. Ishizuka, H. Kasai, H. Oikawa, H. Nakanishi, *Chem. Mater.*, **19**, 1901, 2007

22. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, K. L. Olivier, *J. Polym. Sci., Part A*, **3**, 1373, 1965

23. Y. Nagata, Y. Ohnishi, T. Kajiyama, *Polym. J.*, **28**, 11, 980, 1996

24. H. Colfen, S. Mann, *Angew. Chem. Int. Ed.*, **42**, 2350, 2003

25. G. Li, H. Peng, Y. Wang, Y. Qin, Z. Cui, Z. Zhang, *Macromol. Rapid. Commun*., **25,** 1611, 2004

26. Y. Luo, H. W. Liu, F. X. Jin, C. C. Han, C. M. Chan, *J. Am. Chem. Soc.*, **125**, 6447, 2003

27. J. W. Lauher, F. W. Fowler, N. S. Goroff, *Acc. Chem. Res.*, **41**, 9, 1215, 2008

28. X. Hou, Z. Wang, J. Lee, E. Wysocki, C. Oian, J. Schlak, Q. R. Chu, *Chem. Commun.*, **50**, 1218, 2014

29. A. Pal, P. Voudouris, M. M. E. Koenigs, P. Besenius, H. M. Wyss, V. Degirmenci, R. P. Sijibesma, *Soft. Matter.*, **10**, 952, 2014

30. M. Pietralla, *J. Comput. - Aided. Mat. Des.*, **3**, 273, 1996

31. S. Kawauchi, K. Shirata, M. Hattori, S. Kaneko, R. Miyawaki, J. Watanabe, K. Kimura, *Preprints of 21th Polyimide & Aromatic Polymer conference*, Japan, 2013

32. Y. Yamashita, Y. Kato, S. Endo, K. Kimura, *Makromol. Chem. Rapid Commun.*, **9**, 687, 1988

33. K. Kimura, Y. Kurihara, H. Omori, S. Kohama, S. Yamazaki, Y. Yamashita, *Polymer,* **48**, 3429, 2007

34. K. Kimura, J. H. Zhuang, K. Wakabayashi, Y. Yamashita, *Macromolecules*, **36**, 6292, 2003

35. K. Wakabayashi, T. Uchida, S. Yamazaki, K. Kimura, K. Shimamura, *Macromolecules*, **40**, 239, 2007
36. K. Wakabayashi, T. Uchida, S. Yamazaki, K. Kimura, *Polymer*, **52**, 837, 2011
37. K. Wakabayashi, T. Uchida, S. Yamazaki, K. Kimura, *Macromolecules*, **41**, 4607, 2008
38. M. O. Simon, C. J. Li, *Chem. Soc. Rev.*, **41**, 1415, 2012
39. D. Dallinger, C. O. Kappe, *Chem. Rev.*, **107**, 2563, 2007
40. J. H. Clark, S. J. Taverner, *Org. Process Res. Dev.* **11**, 149, 2007
41. R. A. Sheldon, *Green Chem.*, **7**, 267, 2005
42. W. Wei, C. C. K. Keh, C. J. Li, R. S. Varma, *Clean Techn. Environ. Policy*, **6**, 250, 2004
43. The 12 principles are as follows: prevention, atom economy, less hazardous chemical synthesis, designing safer chemicals, safer solvents, design for energy efficiency, use of renewable feed stocks, reduce derivatives, catalysis, design for degradation, real-time analysis for pollution prevention, inherently safer chemistry for accident prevention. Especially in chemical industry
44. E. J. Beckman, *J. Supercritical Fluids.*, **28**, 121, 2004
45. C. Wheeler, K. N. West, C. L. Liotta, C. A. Eckert, *Chem. Commun.*, 887, 2001
46. C. Capello, U. Fischer, K. Hungerbuhler, *Green Chem.*, **9**, 927, 2007
47. E. Yilgor, G. E. Atilla, A. Ekin, P. Kurt, I. Yilgor, *Polymer*, **44**, 7787, 2003
48. S. Kobayashi, *Proc. Jpn. Acad., Ser. B*, **86**, 338, 2010
49. K. Manabe, X. M. Sun, S. Kobayashi, *J. Am. Chem. Soc.*, **123**, 10101, 2001
50. H. Tanaka, T. Kurihashi, *Polym. J.*, **35**, 359, 2003
51. J. Chiefari, B. Dao, A. M. Groth, *High Perform. Polym.*, **15**, 269, 2003
52. J. Chiefari, B. Dao, A. M. Groth, J. H. Hodgkin, *High Perform. Polym.*, **18**, 437, 2006

53. B. N. Dao, A. M. Groth, J. H. Hodgkin, *Macromol. Rapid Commun*., **28**, 604, 2007

54. B. Dao, J. Hodgin, T. C. Morton, *High Perform. Polym.*, **11**, 205, 1999

55. L. Zhenhai, D. Mengxian, C. Zhongqing, *Thermochimica Acta*., **70**, 71, 1983

56. M. Goyal, T. Inoue, M. Kakimoto, Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 39, 1998

57. K. Itoya, Y. Kumagai, M. Kakimoto, Y. Imai, *Macromolecules*, **27**, 4101, 1994

58. T. Inoue, Y. Kumagai, M. Kakimoto, Y. Imai, J. Watanabe, *Macromolecules*, **30**, 1921, 1997

59. Y. Kumagai, K. Itoya, M. Kakimoto, Y. Imai, *Polymer*, **36**, 14, 2827, 1995

60. Y. Imai, T. Fueki, T. Inoue, M. Kakimoto, *J. Polym. Chem., Part A: Polym. Chem.*, **36**, 1341, 1998

61. H. C. Rain, R. P. Richard, H. Ryder, *Trans. Faraday Soc.*, **41**, 56, 1945

62. R. B. Richard, *Trans. Faraday Soc.*, **42**, 10, 1946

CHAPTER 1

Method for the Morphology Control of Aromatic Polyimide Particles

1-1. Introduction

Aromatic polyimide particles have been used in various fields such as aerospace, electronic devices and membranes due to their high thermal stability, mechanical property and chemical resistance. Recently, morphology control of polyimide particles have been gathering attention, and polyimide particles possessed various morphologies have been prepared such as sphere, hemisphere and hollow and so on. [1-3] Additionally, environmentally benign process to prepare these particles is also required. Among the twelve principles of green chemistry, the utilization of “safer solvents” is very important part in chemical industry, because large amounts of solvents were used for the preparation of these polymer particles. Therefore the morphology architecture for aromatic polyimides in environmentally benign solvent has been eagerly required.

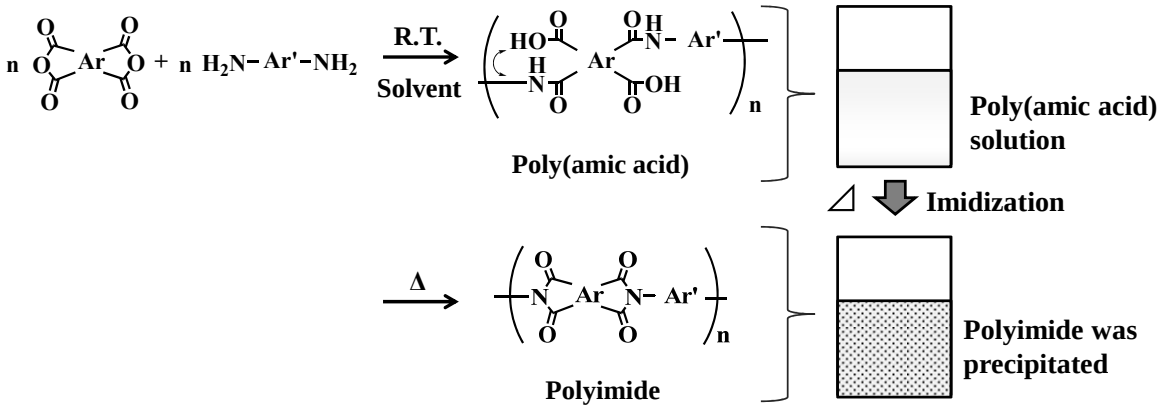
In this Chapter, previous studies about morphology control of aromatic polyimide particles were investigated in order to clarify the usefulness and the importance of the ideas in this thesis. The preparation of aromatic polyimide particles could be roughly categorized into two procedures. One is the precipitation polymerization method, in which polyimide particles were obtained as precipitates *via* phase separation during thermally imidization of aromatic poly(amic acid) precursors, and another is the re-precipitation method, in which polyimide particles were prepared as precipitates by re-precipitation of them. At first, these representative two procedures were summarized. Then, several new and

unique approaches were reviewed such as hydrothermal polymerization of salt monomers [4] and reaction-induced phase separation during solution polymerization. [5] Finally, usefulness and importance of the new morphology architecture for aromatic polyimides in environmentally benign solvent was summarized in conclusion of this Chapter.

1-2. Morphology Control of Polyimide Particles

1-2-1. Precipitation Polymerization Method and Re-Precipitation Method

Almost all aromatic polyimides are insoluble for any organo-solvents due to their rigid structure. Therefore they are usually fabricated by the traditional two-step method *via* the formation of corresponding poly(amic acid) as a soluble precursor. Representative polymers such as PPPI which possesses the highest modules over 500GPa, KAPTON and UPILEX belong to these intractable polyimides, and their fillers have been prepared by precipitation polymerization. [6, 7] Schematic illustration of precipitation polymerization method was depicted in Scheme 1-1. At first, poly(amic acid) as a soluble precursor was obtained by the polyaddition of aromatic tetracarboxylic anhydrides and aromatic diamines in polar aprotic solvents such as *N*-methylpyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc) and so on. Then aromatic polyimide particles were gradually precipitated by heating the solution because the synthesized polyimides were insoluble in these aprotic solvents. Finally, the stepwise heat treatment was carried out up to 400^{o}C to complete the imidization reaction. In this method, various kinds of aromatic polyimide particles were examined, and sheaf-like, spherical and spherulitic crystals were obtained. [8-10] They possessed high crystallinity. Additionally, in



Scheme 1-1 Synthesis of polyimide particles *via* poly(amic acid)s as precursors.

PPPI and KAPTON-type polyimide, their detail crystal structures were investigated by Wide-angle X-ray scattering (WAXS) and selected area electron diffraction (SAED) for the polyimide powders, and their molecules were considered to be regularly oriented to perpendicular to the plate plane direction of leaf crystal composing of spherulites. [8] With respect to the morphology control, Asao reported that their morphology and particle size could be tuned by controlling two parameters such as the difference of solubility parameter between poly(amic acid) and solvent, and the inherent viscosity of poly(amic acid) solution. [10] Although the precipitation polymerization method is interesting in terms of first attempt to control the morphology for rigid aromatic polyimide particles, the particle size or morphology of them were not uniform and the control of morphology was not sufficient.

Re-precipitation method has been attracted and reported in these days. This method could be roughly categorized into two procedures. One is the use of organo-soluble aromatic polyimides.[11-13] Within the past decades, a great variety of organo-soluble aromatic polyimides had been obtained. [14-16] Therefore, many kinds of aromatic polyimide particles were easily prepared by re-precipitation

from the solution of them. Another is the use of poly(amic acid). [17] Although imidization process is needed after re-precipitation of poly(amic acid)s, this approach enables us to prepare intractable polyimide particles same as precipitation polymerization method. In these methods, the solubility of polyimide or poly(amic acid) was lowered by adding poor solvent to the solution or allowing to cool the solution, resulting in causing phase separation in the solution. Schematic illustration of *C*-*T* diagram for the system of amorphous polymer and solvent and that of ternary diagram of polymer / good solvent (GS) / poor solvent (PS) system were depicted in Figure 1-1. The state of homogeneous solution is changed to the metastable state (e.g. point B in Figure 1-1 (a), (b)), consequently phase separation takes place *via* a process of nucleation. The average size of obtained particles was strongly affected by the nucleation rate and the amount of subsequent phase-separating polymers. The size distribution of them is determined by ratio of the nucleation rate to the rate of nucleation growth. Based on the nucleation and growth theory, [18-20] the radii of the critical nuclei r_c, the energy barrier for nucleation ΔG^* and the nucleation rate J, can be expressed as

$$r_c = 2\Omega r_{cf} / kT \ln(1+\sigma) \quad (1)$$

$$\Delta G^* = \frac{16 \pi r_{cf}^3 \Omega^2}{3 [kT \ln(1+\sigma)]^2} \quad (2)$$

$$J = B \exp(-\Delta G^* / kT) \quad (3)$$

where k denotes the Boltzmann's constant, T is the temperature, B is a kinetic parameter and is constant for a given system, Ω is the volume of the growth unit,

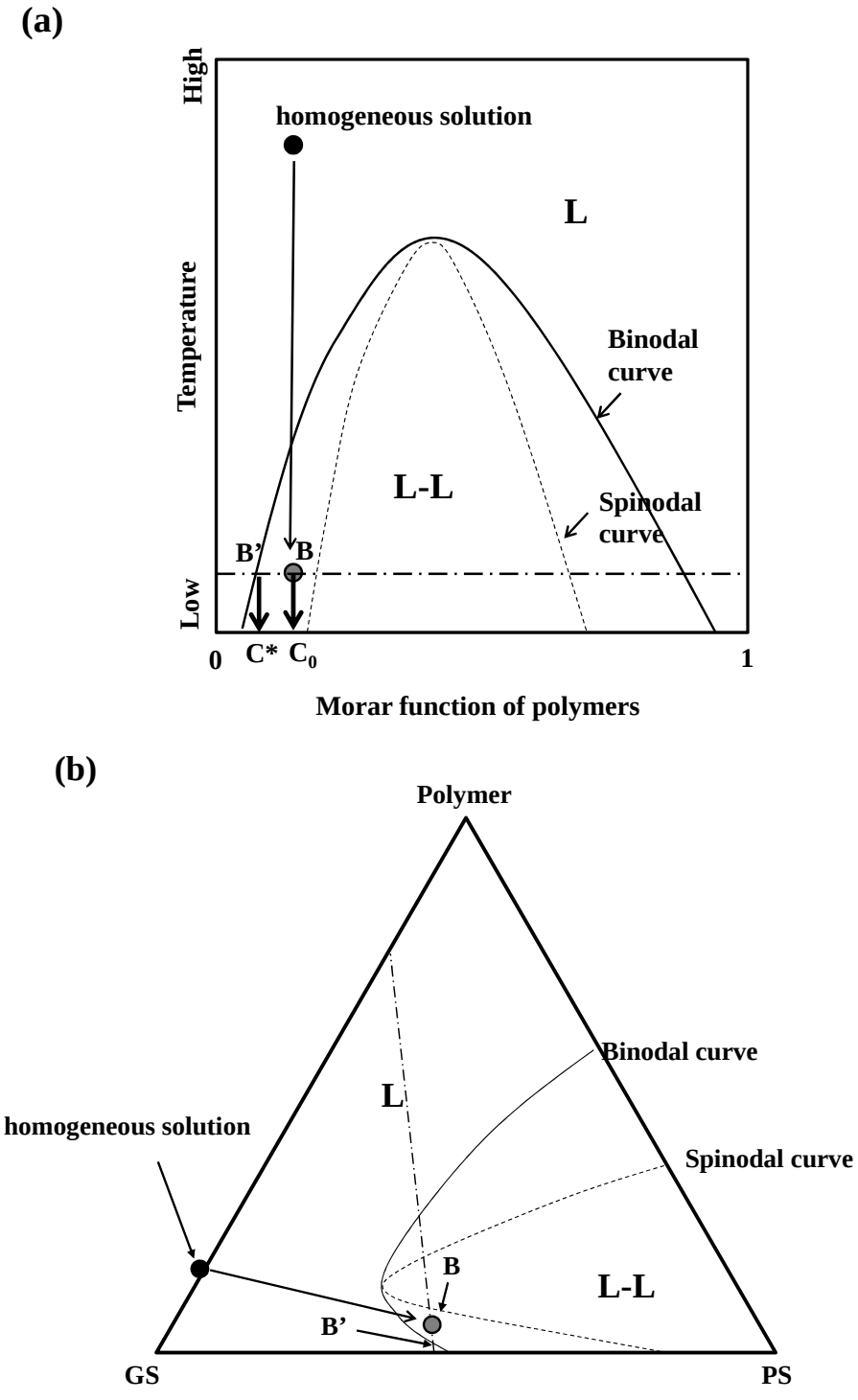
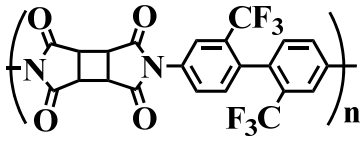
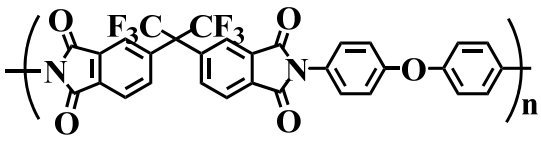


Figure 1-1 Schematic illustration of (a) *C-T* diagram for the system of amorphous polymer and solvent and (b) ternary diagram of amorphous polymer/good solvent (GS) /poor solvent (PS) system. (L: miscible liquid phase, L-L: two immiscible liquid phase)

and γ_{cf} is the surface free energy between the nuclei and the mother phase. σ is the degree of super-saturation [σ = (C_0−C*) /C*], where C_0 is the polymer concentration of the binary or ternary system before the phase separation (e.g., point B, in Figure 1-1), and C* is the polymer concentration of the corresponding continuous phase in equilibrium (e.g., point B' in Figure 1-1). The degree of super-saturation affects nucleation rate according to equation (1)-(3), and hence it is understood as an important factor to determine the particle size. Generally, prevention of droplet coalescence is also important factor to obtain smaller particles. Therefore, a larger degree of super-saturation in phase separation process and lower surface free energy between the nuclei and the mother phase are required to prepare smaller-sized polymer particles in re-precipitation method. Actually, size-controlled polyimide particles were prepared by control of super-saturation [11, 13, 17] and utilizing a surfactant [12]. Beside them, aromatic polyimide particles possessing unique morphology such as porous and hollow particles were prepared by the re-precipitation method.[21-23] With respect to the



Poly [bis(2,2'-trifluoromethyl)benzene cyclobutanetetracarboximide]



Poly[4,4'-oxyphenylene (hexafluoroisopropylidene)dephthalimide]

Scheme 1-2 Chemical structure of porous polyimide particles prepared by re-precipitation method

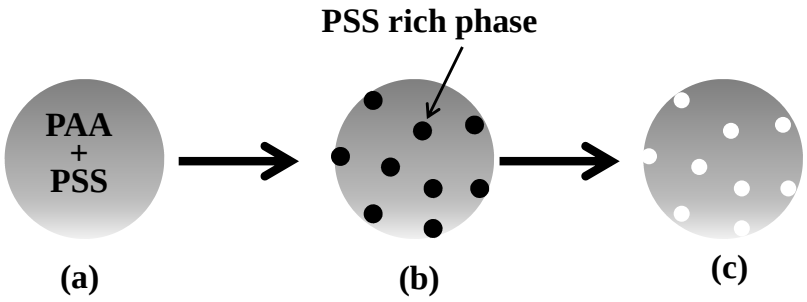
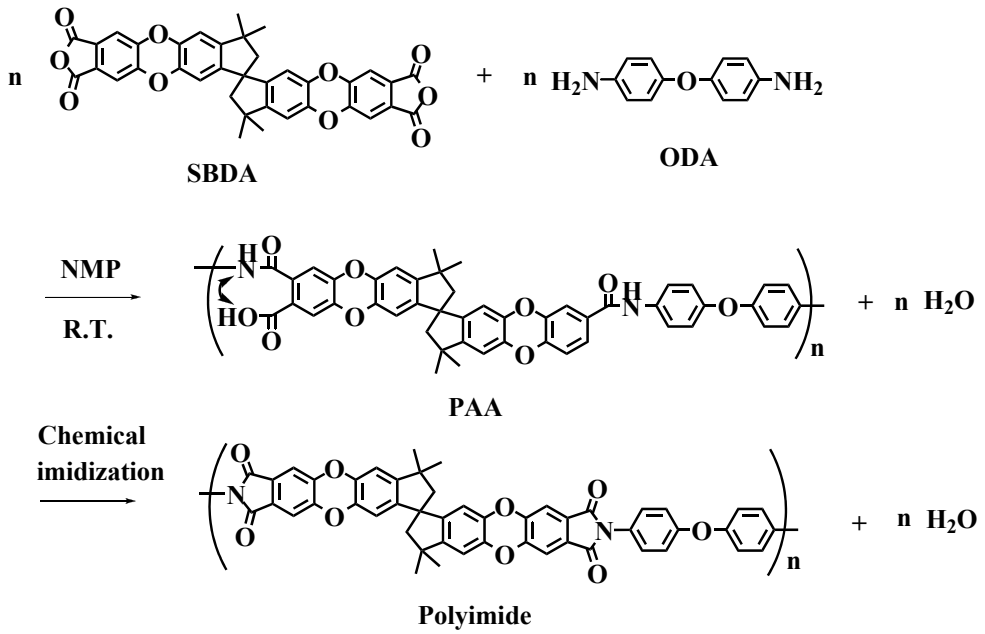


Figure 1-2 Schematic illustration of formation mechanism of porous polyimide particles. (a) A fine droplet of NMP, PAA and PSS formed immediately after mixing of PAA solution and cycrohexane; (b) microphase-separation process of PSS rich phase caused in a fine dloplet of NMP, PAA and PSS; (c) the resulting porous PAA particle prepared by removing PSS.

porous particles, two kinds of aromatic polyimides were examined as depicted in Scheme 1-2. [21, 22] These porous particles were prepared by using the re-precipitation method with poly(sodium-4-styrenesulfonate) (PSS) as the porogen. A solution of poly(amic acid)s (PAA) and PSS in NMP was injected into cyclohexane, which was poor to both PAA and PSS, with vigorous stirring at room temperature to cause the phase separation. After chemical imidization, precipitates were collected and washed with distilled water to remove the PSS. Then, porous PAA particles were finally obtained. Schematic illustration of the formation mechanism was shown in Figure 1-2, and it was considered as follow; the droplets of the mixture of PAA and PSS in NMP were formed *via* the phase separation by mixing the polymer solution and the cycrohexane. Microphase–separation occurred in the droplets and PSS began to precipitate near the surface of the droplets. Finally, the precipitated PSS were removed by washing with water, resulting in the formation of porous particles. Hollow particles of aromatic polyimides prepared from spirobisindane-linked dianhydride (SBDA) and

4-4’-oxydianiline (ODA) were examined, and bowl-like, dimple-like and spherical hollow particles were successfully prepared *via* the phase separation of PAA as shown in Scheme 1-3 and Figure 1-3. [23] At the beginning of the preparation of these hollow particles, NMP droplets containing PAA formed immediately by mixing of PAA solution and cyclohexane which was poor to PAA (Figure 1-3 (a), (b)). Then, PAA rich phases were gradually formed by micro-phase separation from the surface to the center of the droplets, because the NMP molecules gradually diffused into the cyclohexane solution. As a result, microspheres whose surfaces were covered with PAA shells were formed (Figure 1-3, (c)). When the concentration of PAA was enough high, the shell rich in PAA was robust to maintain its morphology after the evaporation of solvent, resulting in the formation of the hollow spheres. On the other hand, when the concentration of PAA was low, the content of PAA in the shell was not sufficient to maintain its morphology during the evaporation of the solvent, and bowl-like and dimple-like hollow spheres were formed (Figure 1-3, (d)). Thus, many kinds of aromatic



Scheme 1-3 Synthesis of PAA and Polyimide from SBDA and ODA

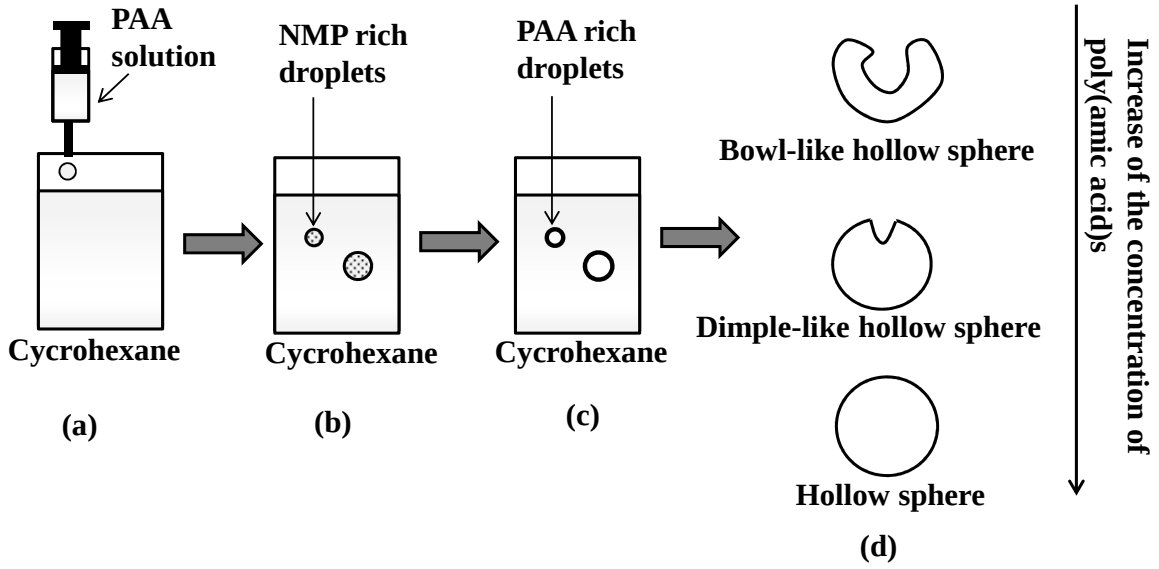


Figure 1-3 Schematic illustration of formation mechanism of various hollow particles. (a), (b) droplets of NMP and PAA were formed immediately after mixing of PAA solution and cycrohexane; (c) PAA rich phases were formed from surface to center of droplets; (d) various hollow spheres were obtained depending on concentration of PAA.

polyimide particles possessing various morphologies were prepared in the re-precipitation method. However, these unique morphologies were achieved *via* liquid-liquid phase separation system, and hence it is difficult to control the higher-order structures of aromatic polyimides. Additionally, the precipitation polymerization method and the re-precipitation method required large amounts of polar aprotic solvent such as NMP, DMAc and DMF, and therefore these methods were not environmentally benign.

1-2-2. Hydrothermal Polymerization of Salt Monomers

From the view point of green chemistry, polyimide synthesis in water had been studied, but the detail of the reaction mechanism had not been clarified. [24-27] Recently, morphology control of aromatic polyimides in water was reported by the research group of Unterlass. [4, 28] Highly crystalline PPPI particles were prepared by means of hydrothermal polymerization of salt monomers derived from pyromellitic acid (PMA) and *p*-phenylene diamine (PPDA). In this method, salt monomers were prepared as precipitates in aqueous solution. Then, the suspension of salt monomer crystals in water was heated up to 200°C in the autoclave under the pressure of approx. 1.7 MPa without stirring. After hydrothermal polymerization, three phases called a-phase, b-phase and c-phase were distinguished in the reaction vessel as shown in Figure 1-4. Two kinds of PPPI particles were obtained from a-phase and b-phase in the reaction vessel, and the total yield of the PPPI particles were 92-98wt% and 2-8wt% respectively. With respect to the morphology, PPPI particles obtained from a-phase was flower-like crystals and those obtained from b-phase was the mixture of flower-like crystals and hollow rhombohedral particles. The external surface of the hollow

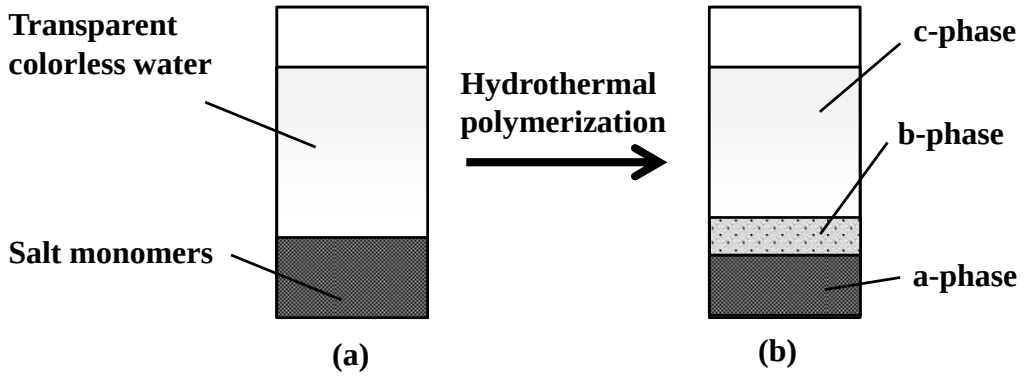


Figure 1-4 Feature of suspension (a) before and (b) after hydrothermal polymerization

rhombohedral particles was covered with small PPPI crystals. Crystal growth mechanism was proposed as depicted in Figure 1-5. During the SSP of the salt monomer crystals, small amount of the salt monomer crystals were dissolved in hot water. Then, oligomers were formed by polymerization in the solution, and both of homogeneous nucleation in the solution and heterogeneous nucleation onto PPPI crystals occurred. In these procedures, the hollow rhombohedral particles were considered to be prepared *via* the process of heterogeneous nucleation onto PPPI crystals prepared by SSP and dissolution of salt monomers. On the other hand, flower-like PPPI crystals might be prepared *via* the process of homogeneous nucleation in the solution and subsequent heterogeneous nucleation onto the nuclei. This method was very interesting in terms of using only water as solvent. However the dissolution of the salt monomers occurred during polymerization and the precipitation of oligomers onto the crystals during polymerization, resulting in the lack of uniformity of morphology and the size of the particles.

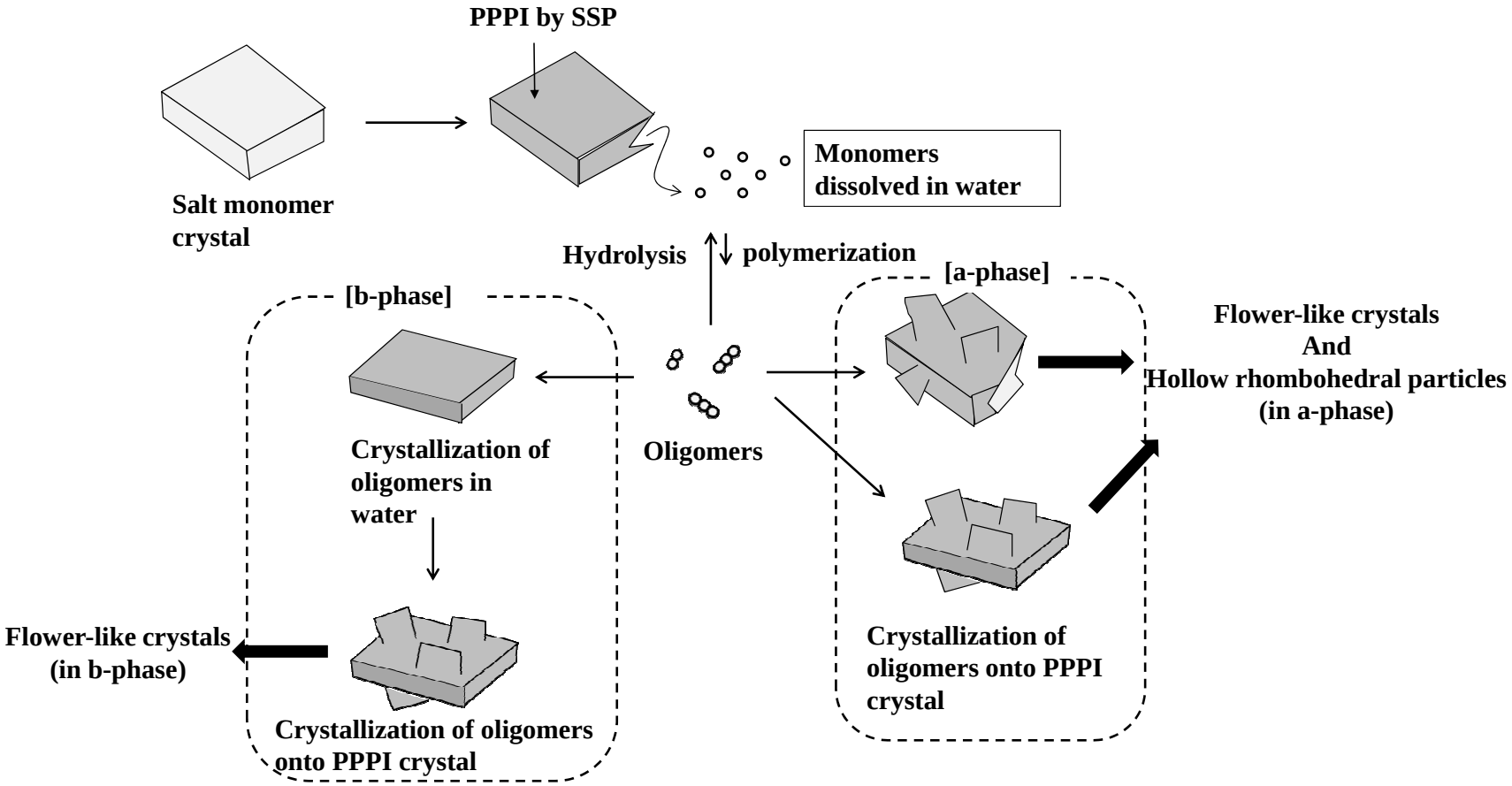
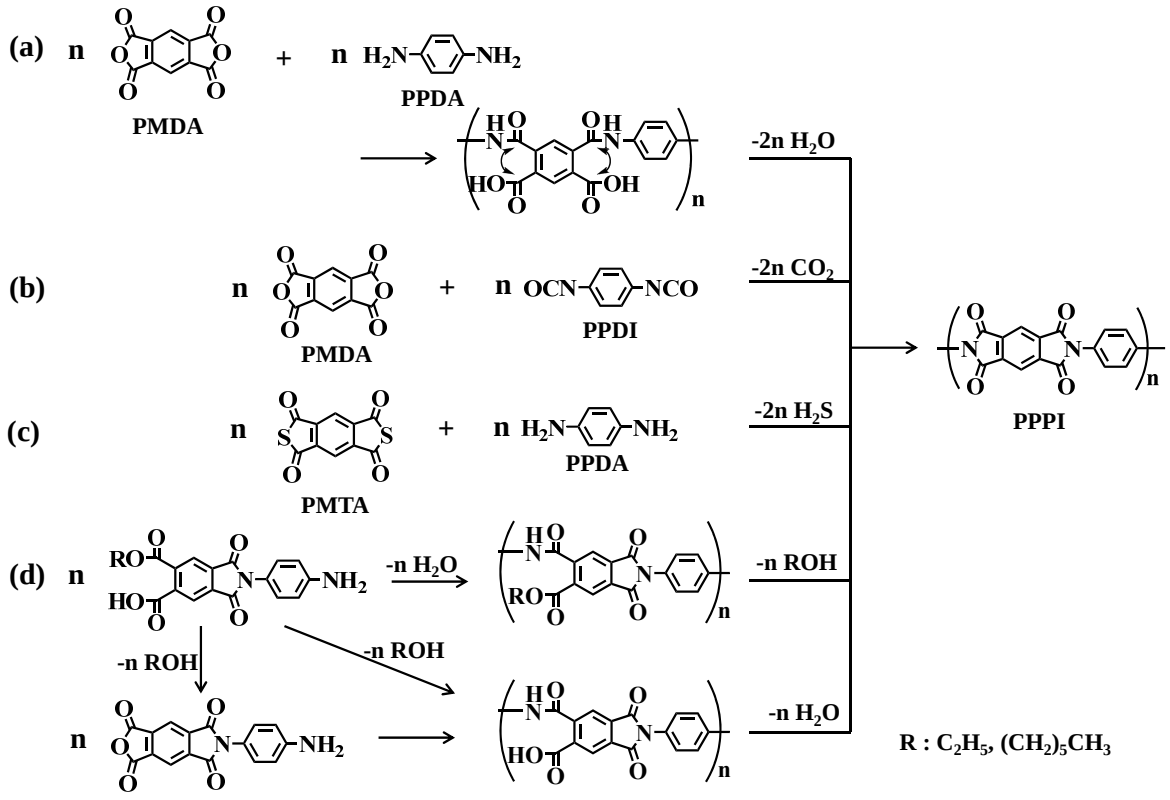


Figure 1-5 Schematic illustration of suggested mechanism of formation of PPPI crystals prepared by hydrothermal polymerization of salt monomers

1-2-3. Reaction-Induced Phase Separation during Solution Polymerization

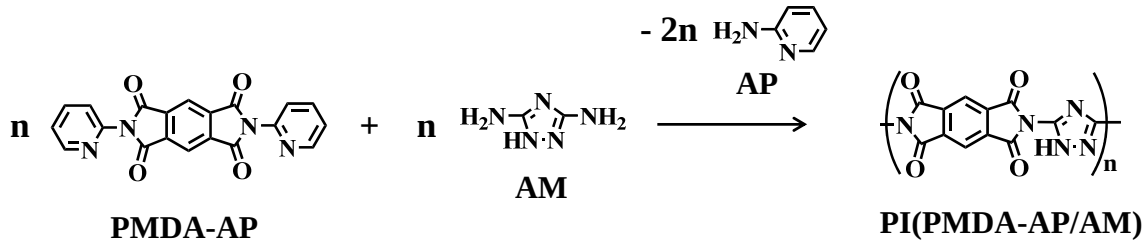
The research group of Okayama University has been studying the morphology control of wholly aromatic polyimides by reaction-induced phase separation of oligomer during solution polymerization. [29-34] In this method, phase separation behavior of oligomers is very important to control the morphology of aromatic polyimide particles. In order to induce the phase separation of oligomers, the solvents which are miscible for monomers and immiscible for oligomers are required. And the phase separation behavior is also affected by the chemical structure of monomers and solvents, and polymerization conditions such as polymerization temperature and concentration of monomers. The PPPI crystals



Scheme 1-4 Synthesis of PPPI from (a) PMDA and PPDA, (b) PMDA and PPDI, (c) PMTA and PPDA and (d) self-condensable monomer (R: C_2H_5, $(CH_2)_5CH_3$)

were prepared from various kinds of monomers as shown in Scheme 1-4.[29-31, 34] In the case of the reaction of PMDA and PPDA, lozenge-shaped crystal, star-like aggregates and microspheres were obtained depending on the polymerization temperature and solvent (Scheme 1-4 (a)). In this polymerization, it was clarified that the degree of imidization of precipitating oligomers affected the morphology of precipitated products. Microspheres were prepared *via* liquid-liquid phase separation of amide-rich oligomers, and another crystals were prepared *via* crystallization of imide-rich oligomers. It had been known that the polyimides are synthesized without the formation of poly(amic acid)s by reaction of either aromatic dianhydrades with aromatic diisocyanates or aromatic dithioanhydrides with aromatic diamines, and hence these reactions were expected that the only imide-oligomers are precipitated by crystallization. Then, the PPPI particles comprised of the plate-like crystals were formed in the polymerization of PMDA and *p*-phenylenediisocyanate (PPDI) and pyromellitic dithioanhydride (PPTA) and PPDA (Scheme 1-4 (b), (c)). In order to induce phase separation of the oligomers posessing high structural homogeneity and stoiciometrically constant of end-groups, the polymerization was examined by using self-condensation monomers. As a result, micro-flowers of the PPPI needle-like crystals were prepared (Scheme 1-4 (d)). Interestingly, the size of the flower-like crystals was controllable by the sturucture of a monomer and the monomer concentration. Additionally, the molecular chain aligned regurally along the long axis of the PPPI needle-like crystals. Based on these results, important factors have been clarifed gradually to control the morphology and higher-order structures of aromatic polyimides. Recently, hollow spheres of aromatic polyimides were also prepared by means of reaction-induced phase separation during solution polymerization as shown in Scheme 1-5. [35] Polymerization of PMDA-AP which was synthesized by

addition reaction of PMDA and 2-aminopyridine and 2-aminopyrimidine (AM) was carried out in DBT at 350°C for 8h. In this study, the elliminating groups of the transimidization were considered as key products to prepare hollow spheres as shown in Figure 1-6. The mechanism was considered as follow. First, gas bubbles derived from elliminated AP by transimidization formed with crystallization of imide oligomers (Figure 1-6 (a)). Then oligomer crystals accumulate onto the gas bubbles, resulting in hierarchical hollow spheres (Figure 1-6 (b)). Finally, they are



Scheme 1-5 Synthesis of PI(PMDA-AP/AM) from PMDA-AP and AM.

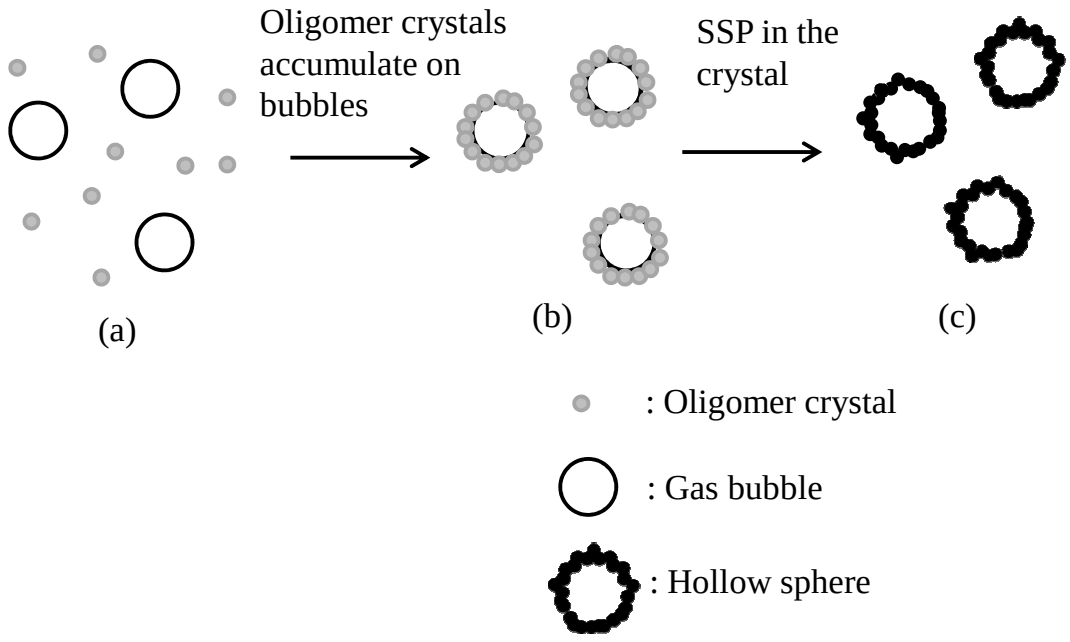


Figure 1-6 Schematic illustration for the preparation of hierarchical polyimide hollow sphere *via* gas bubble template process.

polymerized in solid-state and hollow polyimide particles were finally formed (Figure 1-6 (c)). This method is very interesting in terms of using ellimination groups as key products to control morphology. With respect to the solvent, ethylene glycol (EG) was applied for the reaction-induced phase separation during solution polymerization method from the view point of green chemistry. [36] In this report, salt monomers composed of diethyl pyromellitate and aliphatic diamines and polyvinylpyrrolidone (PVP) as a stabilizer were dissolved into EG and polymerization was carried out at 130^{o}C. And then, aromatic polyimides crystals were obtained. However, the morphology of polyimide particles obtained by this method was not clear in spite of using PVP as a stabilizer.

From these reviews, it was clarified that reaction-induced phase separation during solution polymerization method was unique process which enables us to control not only morphology but also higher-order structures of aromatic polyimides. The morphology and higher-order structures of aromatic polyimide particles were tuned by the chemical structure of monomers and solvents. Therefore, this method implies the possibility of a new method to control the morphology of aromatic polyimides in environmentally benign solvents.

1-3. Conclusions

Four representative methods for the morphology control of aromatic polyimides were investigated such as the precipitation polymerization method, the re-precipitation method, the hydrothermal polymerization of salt monomers and the reaction-induced phase separation during solution polymerization method. In the precipitation polymerization method and the re-precipitation method, it was difficult to control both the morphology and the higher-order structure of aromatic polyimides, and these methods were not environmentally benign processes due to

the usage of large amount of polar aprotic solvents such as NMP, DMF and DMAc. Although the hydrothermal polymerization was very interesting in terms of using only water as solvent, the morphology of obtained polyimide particles was not uniform due to the complicated heterogeneous polymerization system. On the other hand, in the method by means of the reaction-induced phase separation during solution polymerization, it was possible to control both the morphology and higher-order structures. However, large amount of non-polar and high boiling temperature solvent were required in order to achieve morphology control.

From these investigations, it was also confirmed that the phase separation of polymers and oligomers from homogeneous solution was key point for the morphology control of aromatic polyimide particles. Additionally, in order to control the higher-order structures such as crystal structures and molecular orientation of polymers, crystallization is required as phase separation mode. As described before, polyimides or poly(amic acid)s were not dissolved into environmentally benign solvent such as water and alcohol. On the other hand, monomers can be dissolved into various solvents including also water and alcohol. Therefore, two procedures are considered as possible methods to prepare aromatic polyimide particles by phase separation from the aqueous solution. One is preparation of salt monomers derived from aromatic tetracarboxylic acids and tetracarboxylic diamines and subsequent SSP of them. In the hydrothermal polymerization, salt monomers were precipitated and were not dissolved in water. If the morphology of the salt monomer crystals is tuned by crystallization of them and furthermore the morphology of aromatic polyimide particles prepared by SSP reflected the morphology of corresponding salt monomers, it will be facile method to control the morphology of aromatic polyimide particles. Second is use of reaction-induced phase separation of oligomers during solution polymerization.

This method enables us to control both of morphology and higher-order structures of aromatic polyimide particles by tuning of the chemical structures of monomer and solvent. It has been well known that polyimide could be prepared in water via the formation of insoluble part. Therefore, if the monomer structures are modified to dissolve into water and they are polymerized in homogeneous aqueous solution, the reaction-induced phase separation of oligomers will be induced because of low solubility of imide-oligomers in water. Additionally, the morphology and higher-order structures of them will be controlled by the design of water soluble monomer structures.

1-4. References

1. Y. Yang, Z. Jin, Y. Wang, Y. Gu, J. Qin, *Colloid Polym. Sci.*, **291**, 1049, 2013
2. S. Watanabe, K. Ueno, M. Murata, Y. Masuda, *Polym. J.*, **38**, 5, 471, 2006
3. S. Watanabe, T. Ohmura, K. Ueno, M. Murata, Y. Masuda, *Polym. J.*, **40**, 8, 743, 2008
4. B. Baumgartner, M. J. Bojdys, M. M. Unterlass, *Polym. Chem.*, **5**, 3771, 2014
5. K. Kumura, J. H. Zhuang, K. Wakabayashi, Y. Yamashita, *Macromolecules*, **36**, 6292, 2003
6. R. A. Buyny, K. Olesen, US Patent 5248711, 1990
7. T. Folda, J. D. Boyd, H. Tesch, T. Weber, H. G. Recker, European Patent 377194, 1990
8. Y. Nagata, Y. Ohnishi, T. Kajiyama, *Polym. J.*, **11**, 980, 1996
9. F. Basset, A. Lefrant, T. Pascal, B. Gallot, B. Sillion, *Polym. Adv. Technol.*, **9**, 202, 1997
10. K. Asao, H. Ohnishi, H. Morita, *Kobunshi Ronbunshu*, **57**, 5, 271, 2000
11. T. Lin, W. Stickney, M. Rogers, J. S. Riffle, J. E. Mcgrath, H. Marand, *Polymer*, **34**, 4, 772, 1992
12. Z. Chai, X. Zheng, X. Sun, *J. Polym. Sci.; Part B: Polym. Phys.*, **41**, 159, 2003
13. J. Y. Xiong, X. Y. Liu, S. B. Chen, T. S. Chung, *Appl. Phys. Lett.*, **85**, 23, 5733, 2004
14. F. W. Harris, L. H. Lanier, *Structure–solubility relationships in polymers, ed.* F. W. Harris, R. B. Seymour, Academic Press, New York, 1997, p.183
15. D. Kumar, *J. Polym. Sci,: Polym. Chem.*, **22**, 3439, 1984
16. I. K. Spiliopoulos, J. A. Mikroyaunidis, *Polymer*, **37**, 3331, 1996
17. T. Ishuzaka, A. Ishigaki, M. Chatteejee, A. Suzuki, T. M. Suzuki, H. Kawanami, *Chem. Commun.*, **46**, 7214, 2010
18. X. Y. Liu, *J. Chem. Phys.*, **111**, 4, 1628, 1999

19. X. Y. Liu, *J. Chem. Phys.*, **112**, 22, 9949, 2000]
20. X. Y. Liu, *Appl. Phys. Lett.*, **79**, 22, 3603
21. G. Zhao, T. Ishizaka, H. Kasai, H. Oikawa, H. Nakanishi, *Chem. Mater.*, **19**, 1901, 2007
22. G. Zhao, T. Ishizaka, H. Kasai, M. Hasegawa, H. Nakanishi, H. Oikawa, *Polym. Adv. Technol.*, **20**, 43, 2009
23. J. Liu, Y. Yan, Z. Chen, Y. Gu, X. Liu. *Chem. Lett.*, **39**, 1194, 2010
24. J. Chiefari, B. Dao, A. M. Groth, *High Perform. Polym.*, **15**, 269, 2003
25. J. Chiefari, B. Dao, A. M. Groth, J. H. Hodgkin, *High Perform. Polym.*, **18**, 437, 2006
26. B. N. Dao, A. M. Groth, J. H. Hodgkin, *Macromol. Rapid Commun.*, **28**, 604, 2007
27. B. Dao, J. Hodgin, T. C. Morton, *High Perform. Polym.*, **11**, 205, 1999
28. M. M. Unterlass, D. Kopetzki, M. Antonietti, J. Weber, *Polym. Chem.*, **2**, 1744, 2011
29. K. Kimura, J. H. Zhuang, K. Wakabayashi, Y. Yamashita, *Macromolecules*, **36**, 6292, 2003
30. K. Wakabayashi, T. Uchida, S. Yamazaki, K. Kimura, K. Shimamura, *Macromolecules*, **40**, 239, 2007
31. K. Wakabayashi, T. Uchida, S. Yamazaki, K. Kimura, *Polymer*, **52**, 837, 2011
32. K. Wakabayashi, T. Uchida, S. Yamazaki, K. Kimura, *Macromolecules*, **41**, 4607, 2008
33. K. Wakabayashi, S. Kohama, S. Yamazaki, K. Kimura, *Polymer*, **48**, 458, 2007
34. K. Wakabayashi, T. Uchida, S. Yamazaki, K. Kimura, *Macromol. Chem. Phys.*, **212**, 159, 2011
35. Y. Yan, L. Chen, X. Li, Z. Chen, X. Liu, *Polym. Bull.*, **69**, 675, 2012

36. S. Watanabe, A. Wakino, T. Namikoshi, M. Murata, *High Perform. Polym.*, **24**, 8, 710, 2012

CHAPTER 2

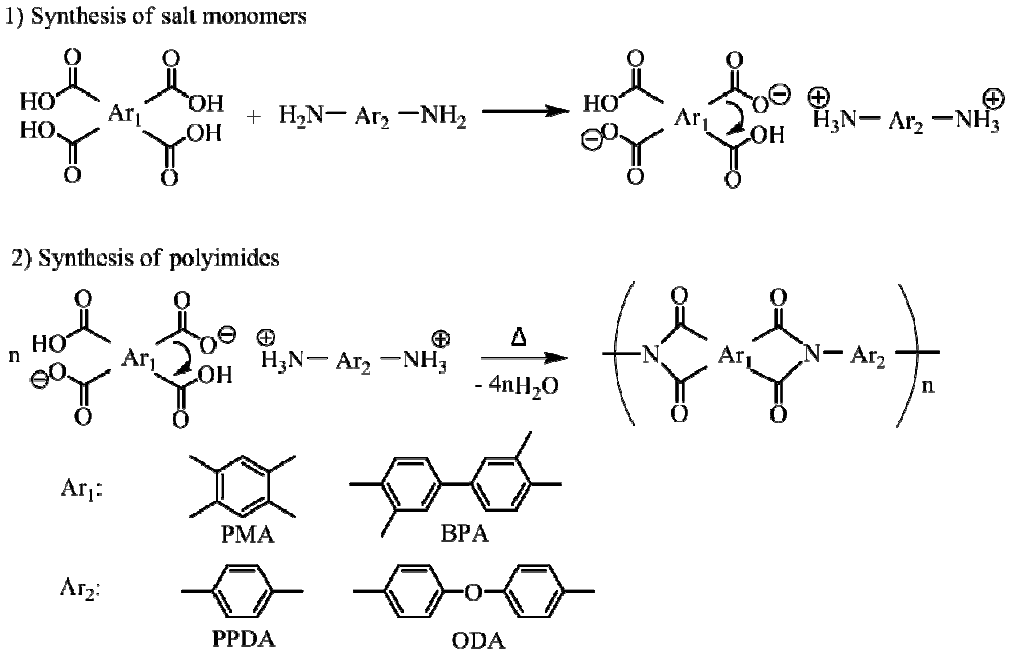
Environmentally Benign Preparation of Aromatic Polyimide Particles by Solid State Polymerization of Salt Monomers and Morphology Control

2-1. Introduction

During past decades, environmentally benign processing has been strongly required to synthesize polymers from the view point of green chemistry. Even in polyimide synthesis, many studies have been reported such as SSP of salt monomers derived from tetracarboxylic acids and diamines and hydrothermal synthesis of the salt monomers. Specifically, high molecular weight KAPTON-type polyimide was prepared by SSP of salt monomers composed of PMA and ODA. The salt monomers were obtained as precipitates by mixing PMA with ODA in methanol, and obtained salt monomers were polymerized in solid state. Recently, the morphology control of aromatic polyimides has been also attracted in addition to above green processing. High crystalline PPPI were prepared in hydrothermal polymerization of salt monomers derived from PMA and PPDA as described in Chapter 1. This method is very interesting in the view point of using only water as solvent. However, the dissolution of the salt monomers occurred during polymerization and the precipitation of oligomers onto the crystals was taken place simultaneously, resulting in the lack of uniformity of the morphology and the size of the particles. On the other hand, the salt monomers derived from aromatic tetracarboxylic acid and 9,9'-bis(4-aminophenyl)fluorene were polymerized in solid state and the obtained polyimide crystals were used as micro-membrane.[1] Even though these procedures have a great potential for the

environmentally benign procedure to prepare the aromatic polyimide particles having clear morphology, the details of this polymerization have not been systematically studied, especially from the view point of the morphology.

In this Chapter, the preparation of aromatic polyimide particles having clear morphology was examined by using the preparation of salt monomer crystals and SSP of them. There are many types of aromatic polyimides represented by poly(4,4'-oxyphenylene pyromelliteimide) and poly(p-phenylene biphenyl tetracarboximide), whose trade names are Kapton (Du Pont Co. Ltd.) and Upilex (Ube Industries Ltd.). They are prepared from PMDA and ODA, and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and PPDA, respectively. These representative aromatic polyimide particles were prepared by two step processes consisted of preparation of salt monomers as precipitates and SSP of them as shown in Scheme 2-1.



Scheme 2-1 Synthesis of aromatic polyimide particles from salt monomers

2-2. Experimental

2-2-1. Materials

PMDA, PPDA and ODA were purchased from TCI Co. Ltd. BPDA was purchased from Sigma-Aldrich Co. Ltd. Pyromellitic acid (PMA) and 3,3',4,4'-biphenyltetracarboxylic acid (BPA) were synthesized by the reflux of PMDA and BPDA with water for 24h. The yields were 79% and 93%, respectively. PPDA and ODA were used as received.

2-2-2. Preparation of salt monomers

Two different procedures were used to prepare salt monomers in this study. The preparation of the salt monomer from PMA and PPDA (SM(PMA/PPDA) was described as typical procedures.

Method A: In a flask equipped with a stirrer, a condenser and the thermometer, a solution of PMA (2.14g, 8.4mmol) in deaerated water (300ml) and a solution of PPDA (0.91g, 8.4mmol) in deaerated water (300ml) were mixed rapidly within 2 sec with stirring, and then the mixture was stirred at 25^{o}C for 1 h under argon flow. White powders were precipitated immediately. They were collected by filtration and dried under vacuum at 50^{o}C for 12 h.

Method B: In a flask equipped with a stirrer, a condenser and the thermometer, a solution of PMA (2.14g, 8.4mmol) in deaerated water (300ml) was slowly added to a solution of PPDA (0.91g, 8.4mmol) in deaerated water (300ml) under stirring for 30 sec, and then the mixture was stirred at 80^{o}C for 1 h under argon flow. White powders were precipitated during the addition of PMA solution. They were collected and dried in the same procedure to Method A.

Salt monomers from other tetracarboxylic acids and diamines were prepared by the

Method A as shown in Table 2-1.

2-2-3. Polymerization of salt monomers

Crystals of salt monomers (1.0g) were put into a crucible, and then it was placed into a DENKEN-HIGHDENTAL Co. Ltd. KDF-MASTER-ACCEL-21 furnace. After replacing air with argon in the furnace, the salt monomers were heated with a heating rate of 2ºC/min. The salt monomers were heated at 220ºC for 3h and then at 400ºC for 3h. After heating, the crucible was allowed to cool to 25^{o}C within 1h and pale yellow or brown polymer powders were collected.

2-2-4. Measurements

Morphology of products was observed on a HITACHI SU-3500 scanning electron microscope (SEM). Samples for SEM were sputtered with aurum by an Eiko IB-3 ion coater. The sputtering of aurum was carried out at 8mA for 1min. under the pressure of 0.1 torr, and 60nm of aurum layer was coated on samples. Observation was performed at 15kV. The size parameters and their coefficients of variation (*Cv*) of the crystals were estimated based on the over 100 sample measurements by KEYENCE VK-X250/260 laser microscope. The polyimide crystal was embedded to carbon film to reduce thermal damage, and then the crystal was cut to the ultra-thin section whose thickness was c.a. 100nm by a HITACHI FB2100 focused ion beam (FIB) system at an acceleration voltage of 40kV. Selected area electron diffraction (SAED) was observed on a JEOL JEM2100F transmission electron microscope (TEM) at an acceleration voltage of 200kV. FT-IR spectra were recorded on a Nicolet MAGNA-IR760 spectrometer. KBr pellets were used for the FT-IR measurements. A powder pattern of wide angle X-ray scattering (WAXS) was recorded on a RIGAKU MiniFlex

diffractometer with nickel-filtered CuKα radiation at 30 kV and 15 mA with a scanning rate of 1°C/min. Thermogravimetric and differential thermal analysis (TG-DTA) was performed on a RIGAKU Thermo plus TGS8120 with a heating rate of 10°C/min in N_2.

2-3. Results and discussion

2-3-1. Preparation of salt monomers

Aromatic polyimides examined in this study were as shown in Scheme 2-1. Salt monomers were prepared by two different procedures and the results were presented in Table 2-1. In this study, salt monomers were abbreviated based on aromatic tetracarboxylic acids and aromatic diamines. For example, the salt monomer prepared from PMA and PPDA was named as SM(PMA/PPDA). Both PMA and PPDA were dissolved in water, and SM(PMA/PPDA) was prepared in

Table 2-1 Preparation of salt monomers

Salt monomer code	Preparation condition				Yield (%)	Morphology
	Method	Solvent	Temp. (°C)	Conc. (mmol/L)		
SM(PMA/PPDA)-1	A	H_2O	25	14	95	Lozenge
SM(PMA/PPDA)-2	A	H_2O	80	14	78	Lozenge
SM(PMA/PPDA)-3	B	H_2O	80	14	95	Lozenge
SM(PMA/ODA)	A	EtOH/H_2O [a)]	25	28	93	Long plate
SM(BPA/PPDA)	A	CH_3OH	50	7	64	Fiber
SM(BPA/ODA)	A	CH_3OH	25	35	87	SP [b)]

a) Mixing ratio = 40/100 wt/wt b) spherical aggregates of plate-like crystals

water. However, ODA and BPA were hardly dissolved in water, and therefore the mixture of ethanol and water or methanol were used as solvents for the preparation of SM(PMA/ODA), SM(BPA/PPDA) and SM(BPA/ODA). Salt monomers were obtained as white precipitates with the yield of 64 - 95%. The yield of salt monomers depended on the preparation conditions. FT-IR spectra of the obtained salt monomers were shown in Figure 2-1. Two ammonium vibration bands were clearly observed at 2590 and 2840cm^{-1}, and the carboxylate stretching bands were observed at 1550-1600cm^{-1}. Intensity of the peaks of the carboxyl group appeared

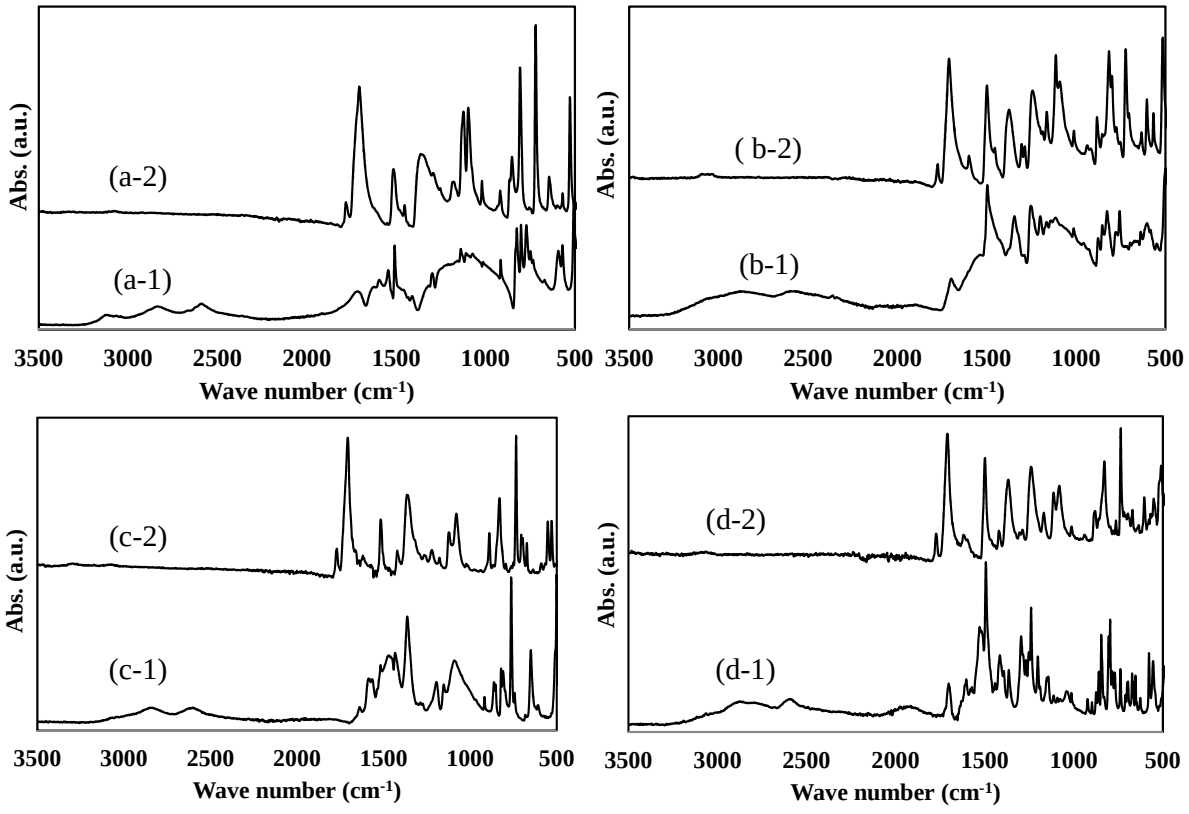


Figure 2-1 FT-IR spectra of salt monomers and corresponding polyimide particles; (a-1) SM(PMA/PPDA)-1, (a-2) PM(PMA/PPDA)-1, (b-1) SM(PMA/ODA), (b-2) PI(PMA/ODA), (c-1) SM(BPA/PPDA), (c-2) PI(BPA/PPDA), (d-1) SM(BPA/ODA) and (d-2) PI(BPA/ODA)

at 1674-1698cm^{-1} in aromatic tetracarboxylic acid decreased in the spectra of salt monomers. These spectra revealed the formation of the salt monomers. Elemental analysis of the salt monomers was performed in order to confirm the chemical composition of them. The results of salt monomers were shown in Table 2-2. The calculated values of SM(PMA/PPDA)-1 are C: 53.04, H: 3.90, N: 7.33 and O: 35.33%. The observed values were C: 51.41, H: 3.67, N: 7.57 and O: 37.35%, and these values were not in good agreement with those of the calculated values. It had been previously reported that the solvent molecules incorporated into the crystals of the salt monomers, [2] and the disagreement might be attributed to the incorporation of water molecules in SM(PMA/PPDA)-1. TG-DTA of salt monomers was performed with heating in N_2. The weight of SM(PMA/PPDA)-1

Table 2-2 Elemental analysis and TG data of salt monomers

Salt monomer code		Elemental analysis (%)				TG (wt%) [a]		
		C	H	O	N	WL	WLc	WLs
SM(PMA/PPDA)-1	Calc.	53.04	3.90	35.33	7.73	21.7	19.9	1.8
	Obs.	51.41	3.67	37.35	7.57			
	Re-calc. [b]	52.09	4.03	36.29	7.59			
SM(PMA/ODA)	Calc.	58.15	3.99	31.69	6.17	19.1	15.9	3,2
	Obs.	55.68	3.96	34.44	5.92			
	Re-calc.	56.76	4.24	33.02	5.97			
SM(BPA/PPDA)	Calc.	60.28	4.14	29.20	6.39	17.2	16.4	0.8
	Obs.	59.66	3.89	30.13	6.32			
	Re-calc.	60.09	4.21	29.36	6.34			
SM(BPA/ODA)	Calc.	63.40	4.18	27.14	5.28	14.5	13.6	0.9
	Obs.	62.54	4.00	28.23	5.23			
	Re-calc.	63.16	4.26	27.35	5.23			

a) WL: Weight loss from 30°C to 450°C measured on a TG-DTA with a scanning rate of 10°C/min in N_2 , WLc: Theoretical weight loss derived from dehydration in the process of polymerization, WLs: WL-WLc b) Corrected assuming that the crystals contained solvent equal amount of WLs in salt monomers

decreased with temperature owing to mainly dehydration and the weight loss at 450^{o}C (WL) were 21.7wt% which was slightly higher than the theoretically calculated weight loss (WLc) of 19.9% to form polyimides. The difference between WL and WLc (WLs) was 1.8%, indicating the incorporation of water molecules in the SM(PMA/PPDA)-1 crystals. The values of C, H, N and O were re-calculated assuming that the crystals contained water molecules equal amount to WLs were C: 52.09, H: 4.03, N: 7.59 and O: 36.29%, and they were closer to the observed values. These values of other salt monomers were also calculated based on the results of TG-DTA as shown in Table 2-2, and these results suggested that solvent molecules were incorporated in salt monomers. WAXS intensity profiles and morphologies of the salt monomers were shown in Figures 2-2 and 2-3, respectively. In Figure 2-2, many sharp diffraction peaks were visualized and diffuse halo of amorphous region was not observed at all. All salt monomers were formed as highly crystalline precipitates. SM(PMA/PPDA)-1 crystals were lozenge-shaped crystals, of which the average longer and shorter length were 39.2 and 10.9μm, respectively. The thickness at the center part was 3.7μm. It was noteworthy that the crystals had symmetrical two projections at the center parts. SM(PMA/ODA) crystals were long plates, of which the average longer and shorter length were 92.3 and 12.0μm, respectively. The thickness was 7.1μm. SM(BPA/PPDA) crystals were fibrillar, of which the cross sections were quadratic. The average width of SM(BPA/PPDA)crystals was 1.7μm, but the length of them was hardly measured because of the intricate entanglement. SM(BPA/ODA) crystals were spherical aggregates of plate-like crystals like spherulites. SM(PMA/PPDA)-1, 2 and 3 were prepared by different conditions and methods. They exhibited lozenge-like morphology, whereas the shapes of them were quite different as shown in Figures 2-4 and 2-5. The thickness of SM(PMA/PPDA)-1

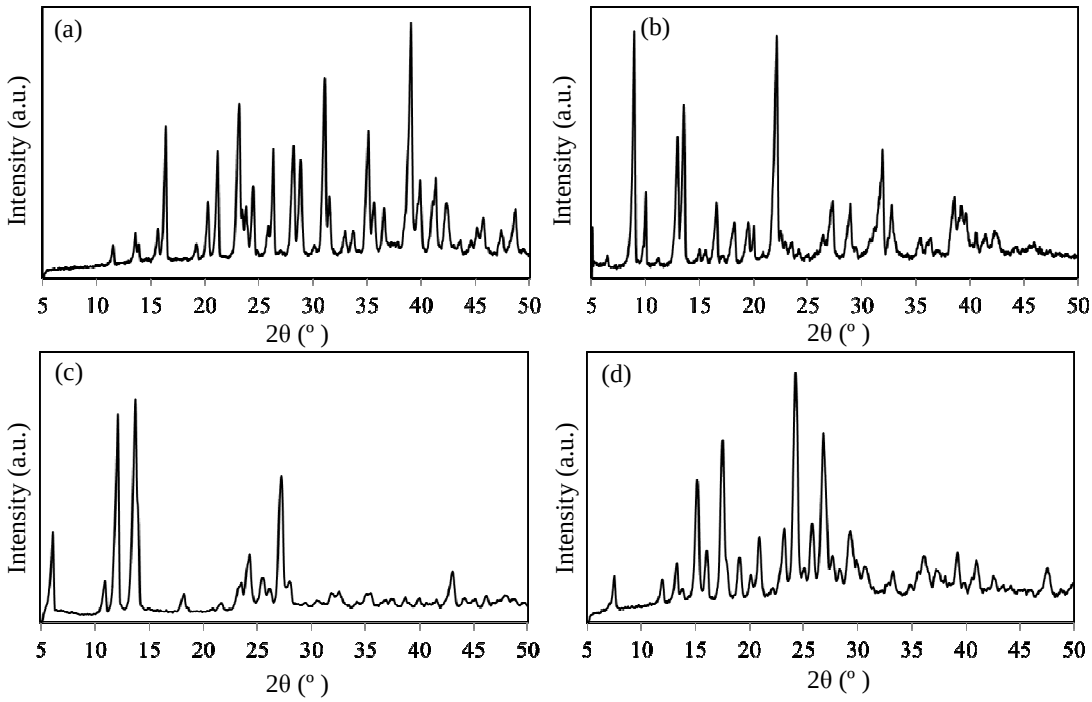


Figure 2-2 WAXS intensity profiles of salt monomers; (a) SM(PMA/PPDA)-1, (b) SM(PMA/ODA), (c) SM(BPA/PPDA) and (d) SM(BPA/ODA)

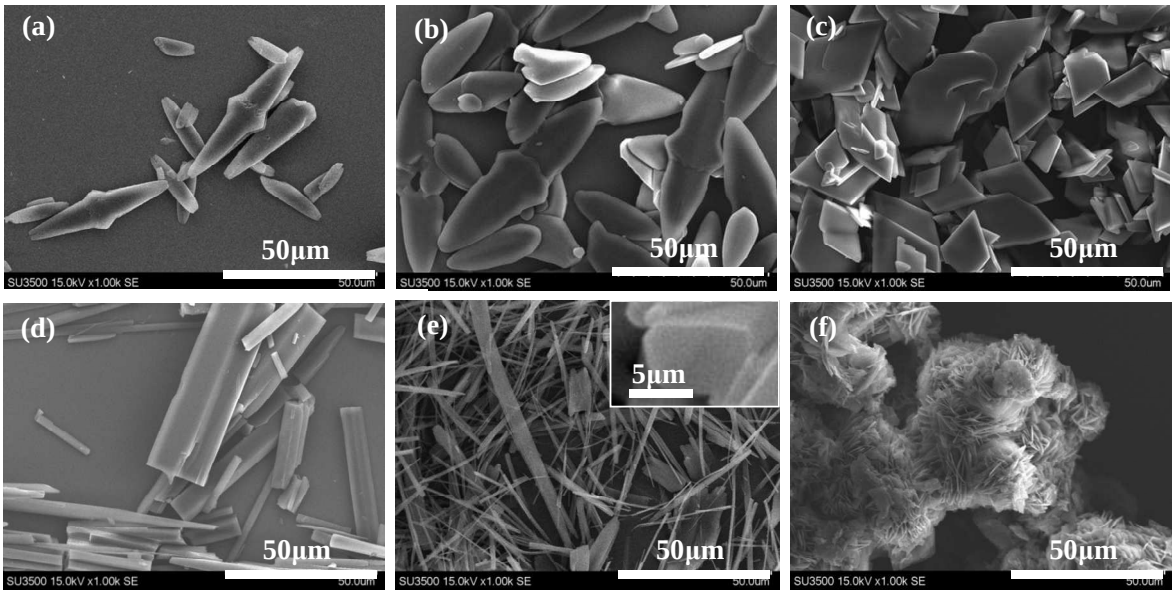


Figure 2-3 Morphology of salt monomer crystals; (a) SM(PMA/PPDA)-1, (b) SM(PMA/PPDA)-2, (c) SM(PMA/PPDA)-3, (d) SM(PMA/ODA), (e) SM(BPA/PPDA) and (f) SM(BPA/ODA)

and -2 crystals prepared by the method A became thinner from the center to the edge, and they were tapered. In contrast to this, SM(PMA/PPDA)-3 crystals prepared by the method B exhibited very clear lozenge-like morphology and they did not have symmetrical two projections at the center parts observed in the SM(PA/PPDA)-1 and -2 crystals. Further, they were not tapered and depicted as lozenge-shaped plate-like crystals. The average sizes and their distribution were distinctly different. The average longer, shorter length and thickness of center part of the SM(PMA/PPDA)-1 crystals were 39.2 (*Cv* 28%), 10.9 (*Cv* 24%) and 3.7μm, respectively. Those of the SM(PMA/PPDA)-2 crystals were 53.6 (*Cv* 21%), 15.8 (*Cv* 27%) and 4.9μm, respectively, and their average size was 1.3 - 1.4 times larger

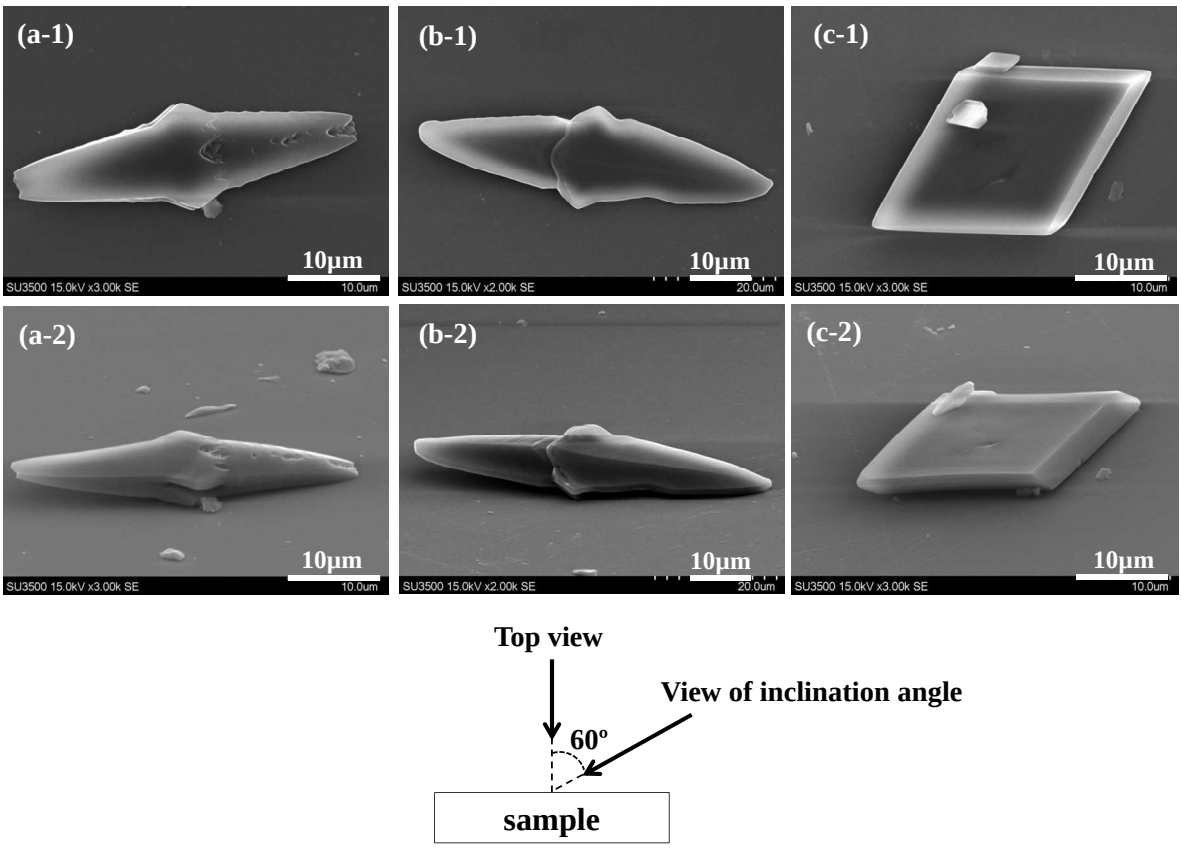


Figure 2-4 Top view (-1) and inclined view (-2) of (a) SM(PMA/PPDA)-1, (b) SM((PMA/PPDA)-2 and (c) SM(PMA/PPDA)-3

than that of SM(PMA/PPDA)-1. The average longer, shorter length and thickness of the SM(PMA/PPDA)-3 crystals were 28.0 (*Cv* 38%), 17.1 (*Cv* 32%) and 2.5μm, respectively. The size of the SM(PMA/PPDA)-3 crystals was smaller, but the *Cv* values were larger. These results imply that the growth feature of the SM(PMA/PPDA)-1 and -2 crystals might be basically similar, but that of the SM(PMA/PPDA)-3 crystals was slightly different. Generally, the degree of the super-saturation affects both the number of nuclei and the crystal growth rate. [3] The degree of the super-saturation at 80ºC was lower than that at 25ºC, and therefore the number of nuclei prepared at 80ºC was smaller than those at 25ºC, resulting in the formation of larger size crystals. The SM(PMA/PPDA)-3 crystals prepared at 80ºC in method B were flat lozenge-shaped plate-like crystals as mentioned above. In method B, the degree of the super-saturation at the initial stage of the preparation was smaller than that in method A. Additionally, the degree of super-saturation was roughly kept because the PMA solution was continuously supplied into the PPDA solution, bringing about the formation of the crystal having clear lozenge-shape morphology. The addition of the PMA solution into the solution of PPDA after the nucleation possibly cause nucleation besides crystal growth if the degree of super-saturation is enough high, resulting in the increase in the *Cv* values. The morphology and the size of salt monomers are susceptible to not only the chemical structure but also crystallization condition.

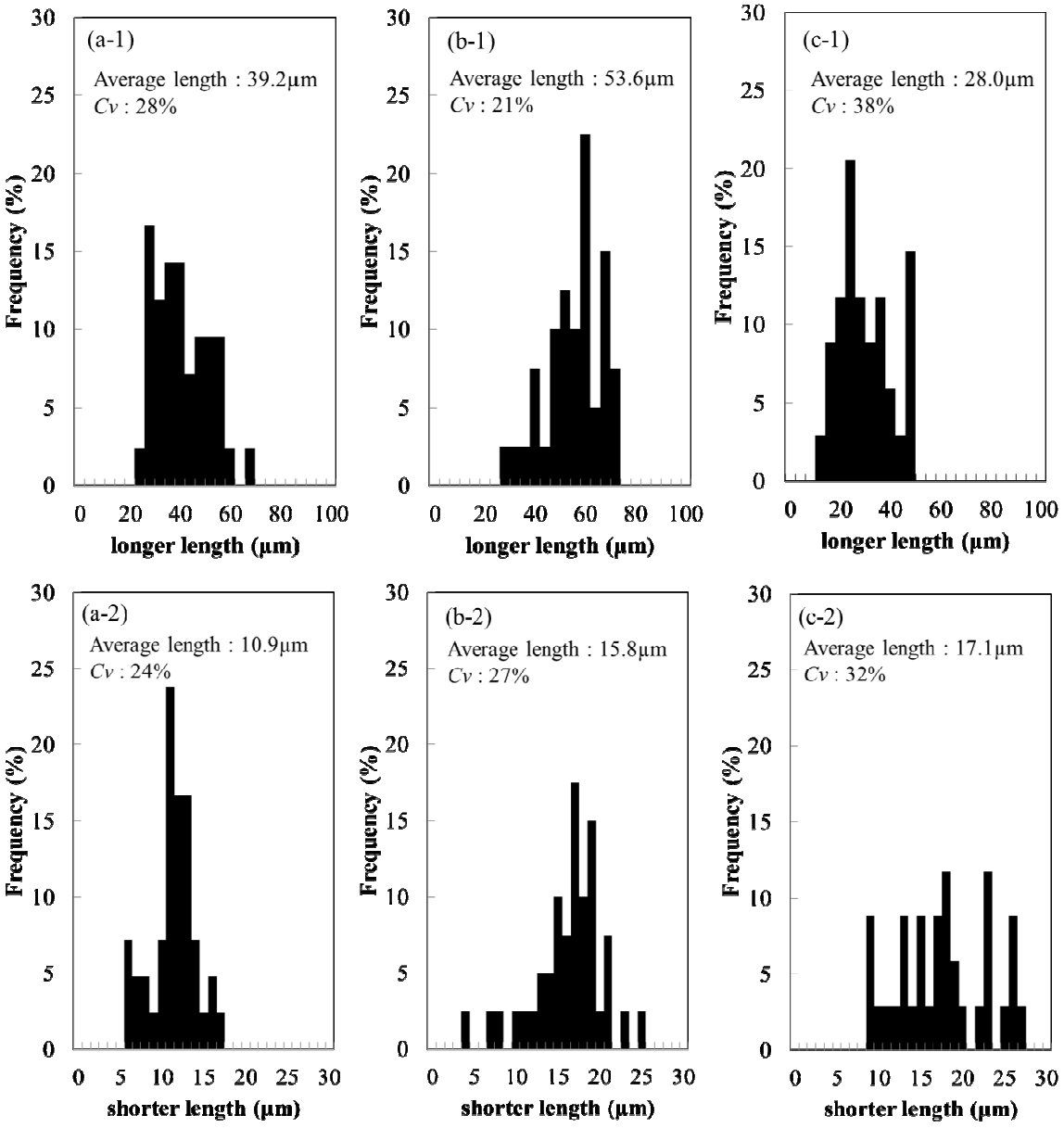


Figure 2-5 Distribution diagrams of longer (-1) and shorter (-2) length of (a) SM(PMA/PPDA)-1, (b) SM(PMA-PPDA)-2 and (c) SM(PMA/PPDA)-3

2-3-2. Polymerization of salt monomers and morphology of polyimides

Polyimides were abbreviated by using corresponding monomers. For example, PI(PMA/PPDA) stands for the polyimide prepared from SM(PMA/PPDA). In order to determine the polymerization condition, TG-DTA analysis was first performed. The profiles of SM(PMA/PPDA)-1 were shown in Figure 2-6. Weight loss started gradually at ca. 150°C and finished at ca. 350°C in the heating profile of Figure 2-6 (a). In the DTA profile, two endothermic peaks were mainly observed at 220°C and 252°C. These endothermic peaks were not melting transition and they were attributed to the elimination of water *via* two different dehydration reactions. The weight loss at lower temperature was mainly owing to the formation of the amide linkage and that at higher temperature was

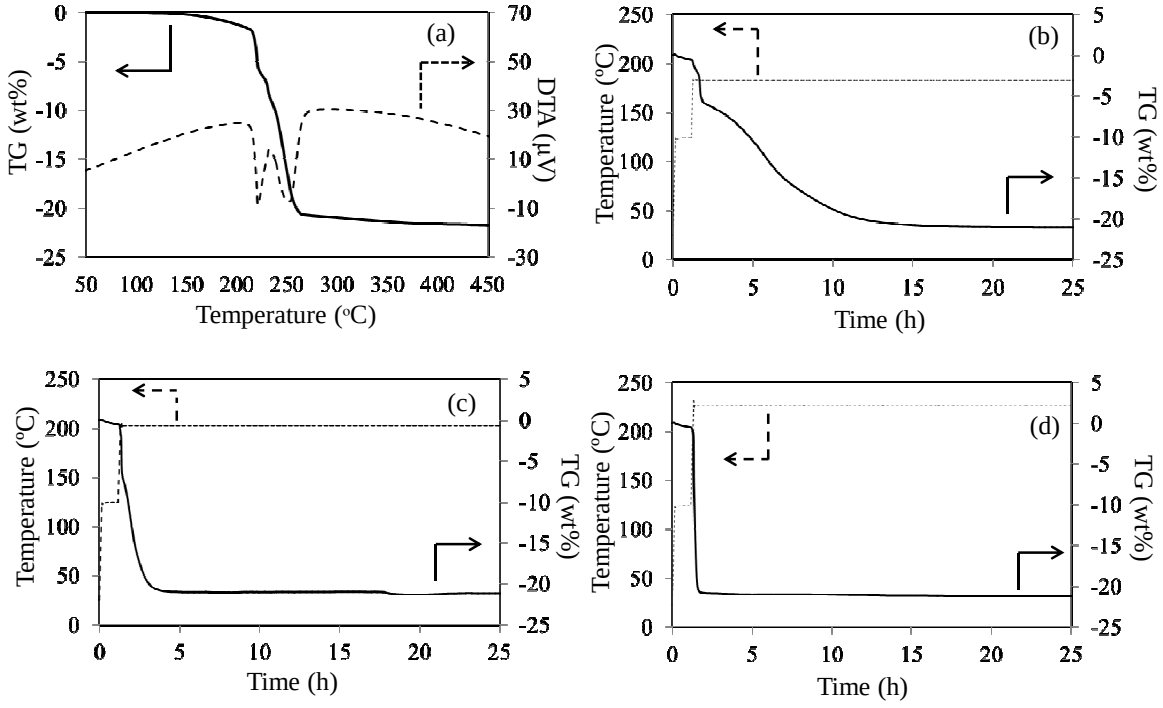


Figure 2-6 TG-DTA profiles of SM(PMA/PPDA)-1; (a) heating profile with a rate of 10°C/min in N_2, and isothermal profiles at (b) 180°C, (c) 200°C and (d) 220°C in N_2

mainly owing to the cyclization of amic acid moieties to form imide linkages. Based on these results, TG analysis of SM(PMA/PPDA)-1 was isothermally carried out at 180, 200 and 220ºC in N_2 as shown in Figure 2-6 (b) – (d). Weight decreased with time by the dehydration and weight loss became constant at ca. 21%. It is noteworthy that the weight loss occurred more rapidly at higher temperature. The weight loss reached to 20.8% within 30 min and then it became constant at 21.0% at 2.8 h at 220ºC. Therefore, the salt monomers were polymerized at 220 ºC for 3h and then at 400 ºC for 3h to complete the imidization under argon flow. White salt monomers turned to pale yellow or brown powders during polymerizations. FT-IR spectra of the polymerized particles are shown in Figure 2-1. Ammonium vibration bands at 2590 and 2840cm^{-1} and the carboxylate stretching bands at 1550-1600cm^{-1} of the salt monomers disappeared after the polymerization, and the imide carbonyl stretching bands were newly observed at 1784 and 1722 cm^{-1}. The degree of imidization (DI) calculated by FT-IR spectra [4] and the temperature of 5wt% loss (Td_5) measured by TG in N_2 of polyimides were shown in Table 2-3. The bands of the amic acid moiety were not visualized at all and the DI was almost equal to 1.0, indicating that the polymerized particles were fully cyclized polyimides. Td_5 values were 569 - 612ºC, depending on the polymer structure. These results reveal the formation of high molecular weight polyimides.

Table 2-3 Characterization of polyimide crystals

Polymer code	DI [a)]	Td_5 [b)] (ºC)	Morphology
PI(PMA/PPDA)-1	1.0	612	Lozenge
PI(PMA/ODA)	1.0	576	Long plate
PI(BPA/PPDA)	1.0	593	Fiber
PI(BPA/ODA)	1.0	569	SP [c)]

a) Degree of imidization calculated by FT-IR spectra b) Temperature of 5 wt% loss measured on a TG with a heating rate of 10ºC/min in N_2 c) spherical aggregates of plate-like crystals

WAXS intensity profiles and the morphologies of the polyimide particles were shown in Figures 2-7 and 2-8, respectively. The morphologies of the polyimide particles were very clear as well as those of the salt monomers. It is very noteworthy that the morphologies and the size of the polyimides were almost the same as those of the corresponding salt monomers. The polymerization proceeded with maintaining the morphology of the salt monomers. With respect to the WAXS intensity profiles, diffraction peaks were observed, even though the amorphous halos were seen. The crystallinity of polyimide particles became lower than that of the salt monomers. All diffraction peaks were assignable by the orthorhombic unit cell of polyimides previously reported [5-8] as indexed besides PI(BPA/ODA) because the crystal structure of PI(BPA/ODA) had not been determined yet. All polyimide crystals prepared in this study had the same crystal structures as previous crystals and novel crystal structure was not observed. With respect to PI(PMA/PPDA)-1, sharp diffraction peaks were observed and the broad halo derived from amorphous region was hardly seen in the profile, indicating quite high crystallinity. The crystallinity of PI(PMA/ODA) and PI(BPA/PPDA) was relatively lower than that of PI(PMA/PPDA)-1. Amorphous halo was strongly observed, but diffraction peaks were visualized in the profile of PI(BPA/ODA). The crystallinity of PI(BPA/ODA) was the lowest owing to the unsymmetrical structure based on the rotation of BPA moiety and the ether linkage, but it was crystalline. In order to investigate the molecular orientation in the crystal, the selected area electron diffraction (SAED) of the PI(PMA/PPDA)-1 crystal was observed as shown in Figure 2-9. The crystal was sliced perpendicular to the plate-plane, which was the thickness direction, by following three steps. First, carbon was deposited to a part of the crystal surface in order to reduce thermal damage during etching process from focused ion beam (FIB) as shown in Figure

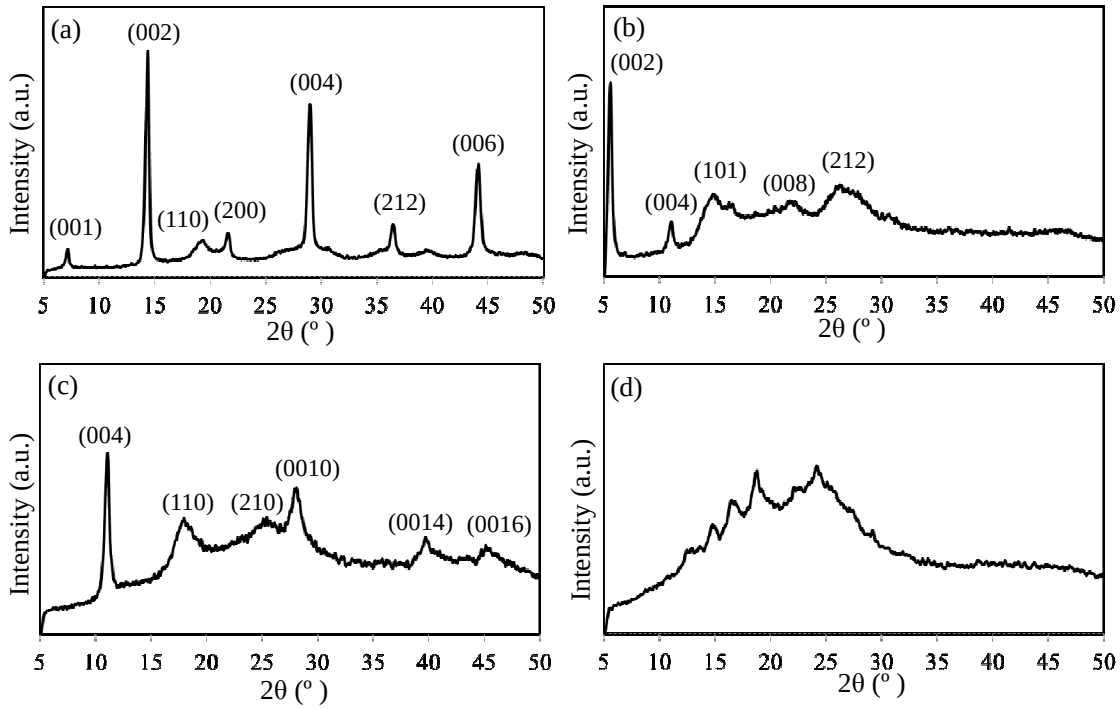


Figure 2-7 WAXS intensity profiles of polyimide particles; (a) PI(PMA/PPDA)-1, (b) PI(PMA/ODA), (c) PI(BPA/PPDA) and (d) PI(BPA/ODA)

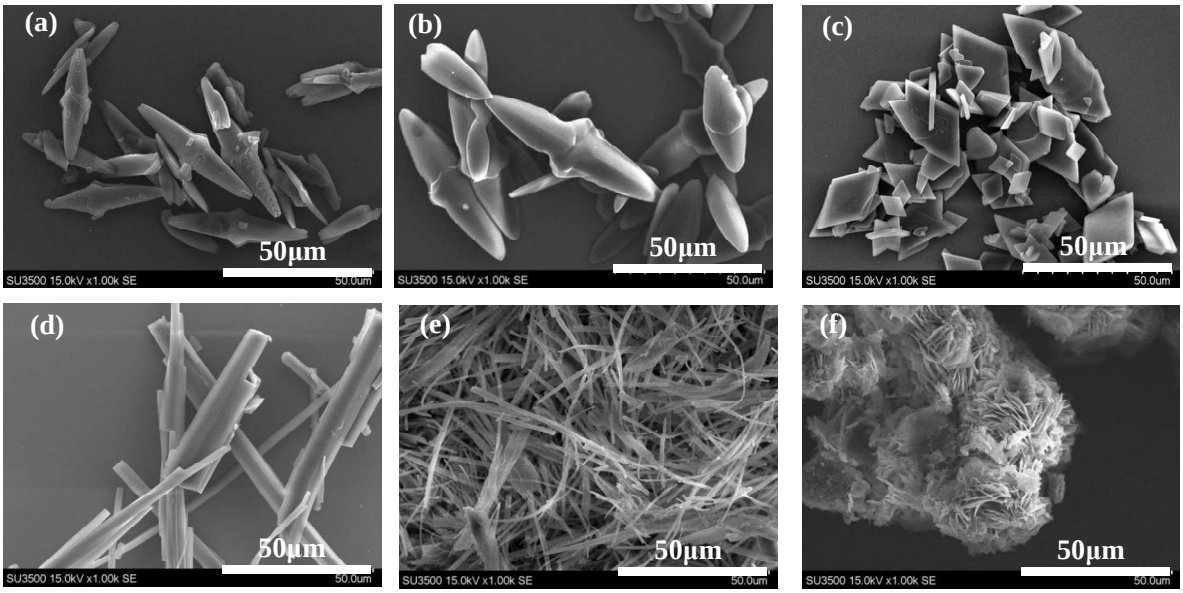


Figure 2-8 Morphology of polyimide crystals; (a) PI(PMA/PPDA)-1, (b) PI(PMA/PPDA)-2, (c) PI(PMA/PPDA)-3, (d) PI(PMA/ODA), (e) PI(BPA/PPDA) and (f) PI(BPA/ODA)

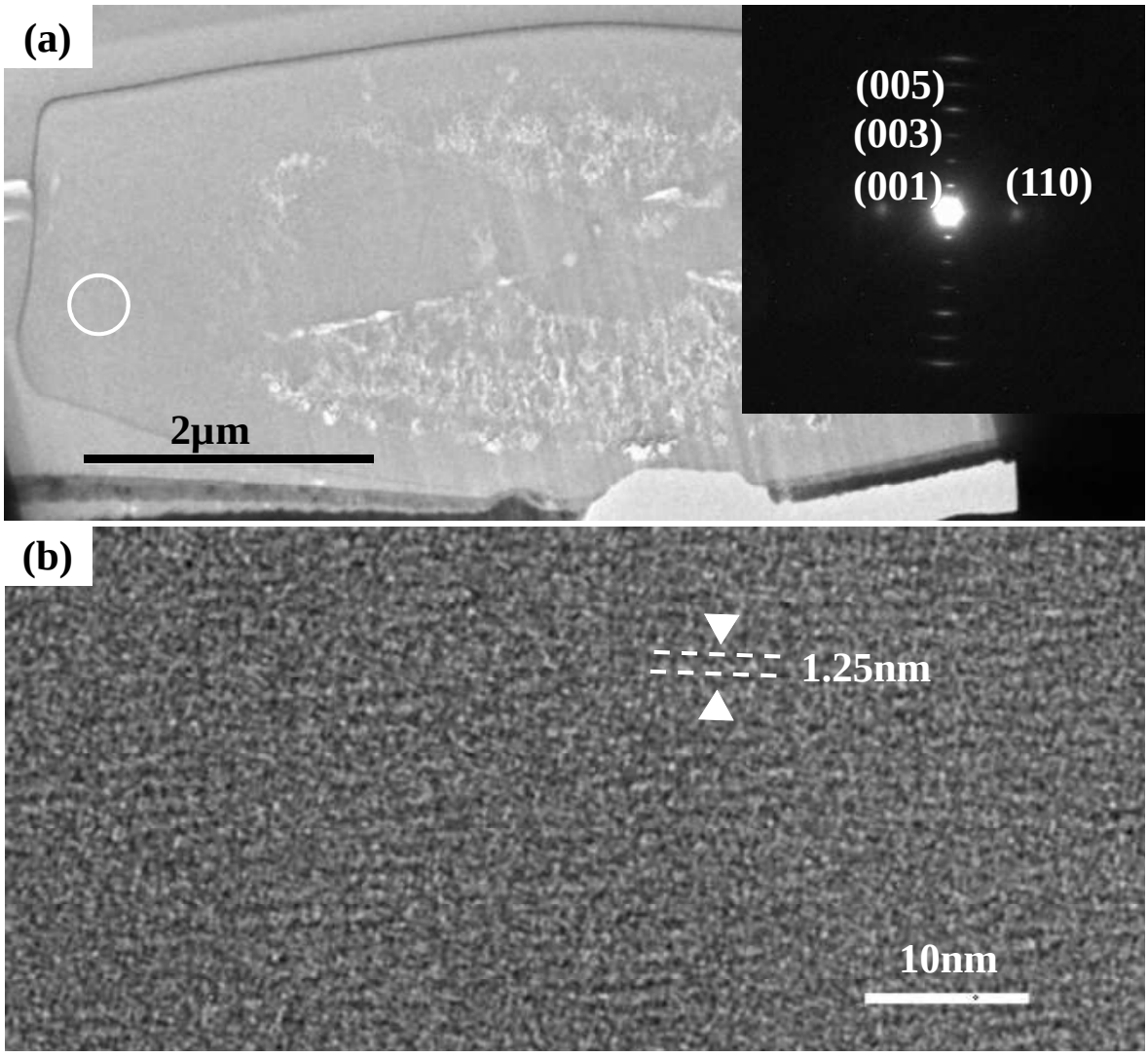


Figure 2-9 TEM image of sliced crystal of PI(PMA/PPDA)-1 crystal and SEAD taken by incident of electron beam perpendicular to plane of the crystal (a), and high resolution TEM of selected area (b).

2-10, (a), (b). Second, the crystal was absolutely etched by FIB beside carbon deposition area, and then sliced plate whose thickness was 3.6μm was obtained as shown in Figure 2-10, (c). Finally, that sliced plate were additionally etched from the perpendicular to the sliced plane, and ultra-thin sample whose thickness was c.a. 100nm was obtained as shown as Figure 2-10, (d). The SAED was taken by the

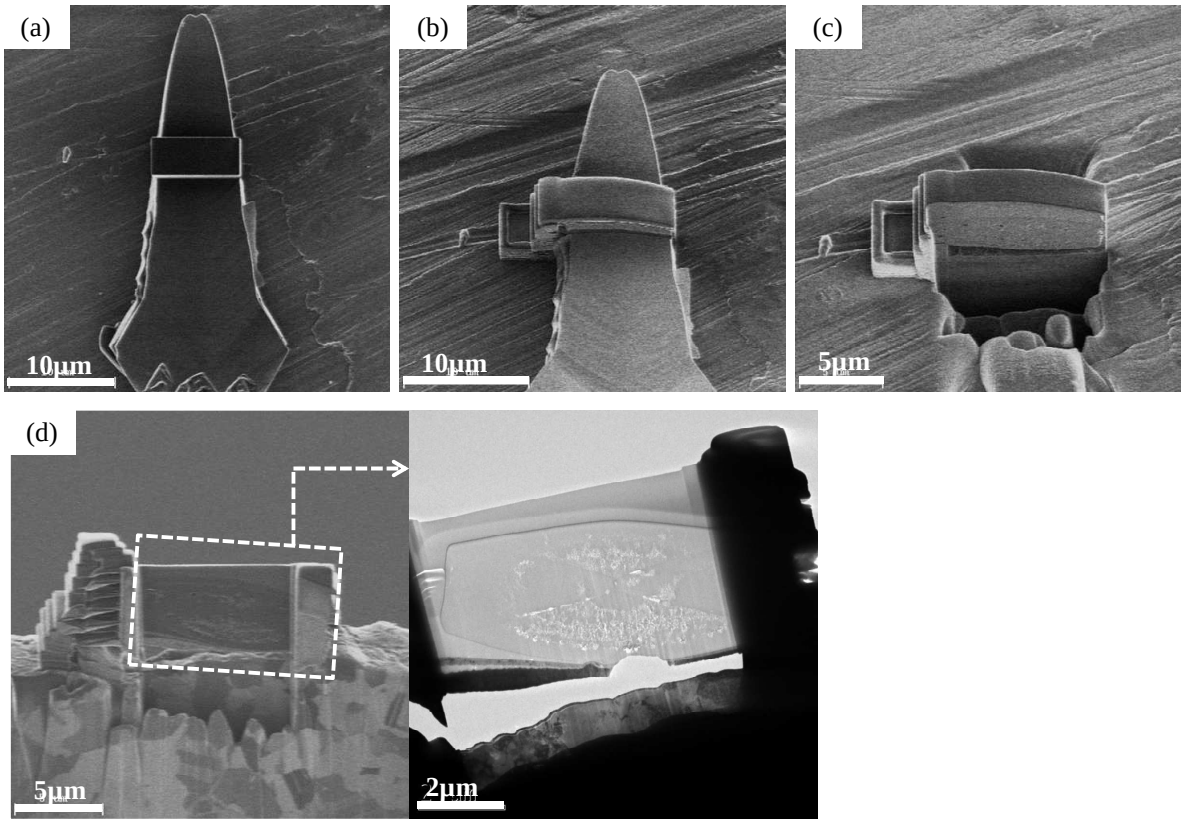


Figure 2-10 Top view of scanning ion microscope (SIM) image of cut off area of PI(PMA/PPDA)-1 crystal (a), inclined view of SIM image of cut off area of that crystal (b), sliced sample prepared by cut off by FIB (c) and side view of SIM and TEM image of ultra-thin section prepared by additional etching of sliced plane by FIB (d).

irradiation of electron beam perpendicular to the sliced plane. Many spots were observed from lower to higher-ordered diffractions, and they could be indexed with the previously reported orthorhombic unit cell of poly(1,4-phenylene pyromelliteimide). [5, 6, 9] The meridian direction of the pattern was identical with the thickness direction of the crystal, indicating that the polymer chains aligned along the thickness of the crystal. The refractions of 00ℓ were strong but slightly diffused. This broadening of the spots on the meridian direction might be

attributed to the orientational fluctuation of crystallites, the axial shifted polymer molecules structure, [10-12] or the crystal size effect. [13] On the other hand, the spots on the equatorial direction were not so strong and more diffused. This result indicates that crystal structure of radial direction is disordered. In the polymerization process, large conformational change might be brought out due to the elimination of water molecules from the crystal, resulting in disordered structure to radial direction. A high resolution transmission electron micrograph was also taken. Lattice fringes were clearly observed running perpendicular to the thickness direction of the crystal, and the spacing of the lattice fringes was ca. 1.25 nm, corresponding to the *d*-spacing of 001. These results strongly supported that polymer molecules aligned perpendicular to the plate-plane of the crystal, corresponding to the direction of the thickness. The regions where the lattice fringes were tilted and distorted were observed, bringing about the diffused refractions of 00ℓ discussed above.

The changes in the WAXS intensity profile and the FT-IR spectrum of PI(PMA/PPDA)-1 were examined at the early stage of polymerization to understand the polymerization behavior. The results were shown in Figure 2-11. The weight loss was also monitored and it was 3.2% at 3 min, 12.3% at 10 min and 20.8% at 30 min. In the WAXS profiles, the intensity of the characteristic peaks at 16.4°, 23.1°, 31.0°, 35.1° and 39.1° of SM(PMA/PPDA)-1 were relatively decreased, and sharp peaks of 00ℓ planes and broad peaks of *hk*0 planes of PI(PMA/PPDA)-1 appeared gradually with time. The profile after 30 min was close to that of PI(PMA/PPDA)-1, even though the weak peaks of salt monomers were observed. This change in the WAXS intensity profiles indicated that the polymerization underwent in the solid state, and hence the morphology of the salt monomers remained after the polymerization. With respect to the change in the

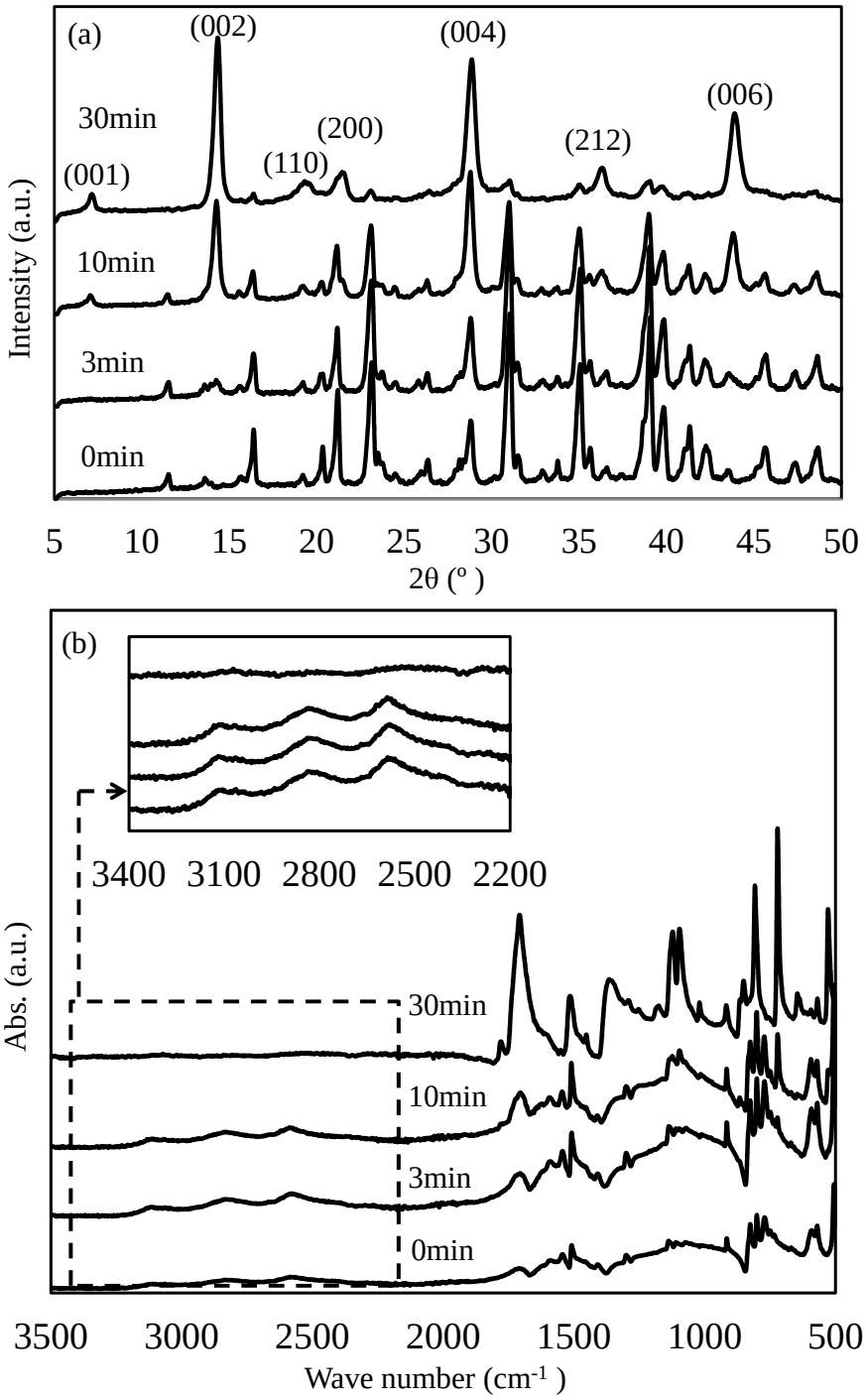


Figure 2-11 Changes in (a) WAXS intensity profiles and (b) FT-IR spectra of SM(PMA/PPDA)-1 with time at 220ºC

FT-IR spectra, the amide carbonyl were not detected from early stage such as 3min and 10min, even though the dehydration was observed described before. Additionally the imide carbonyl stretching bands were also observed at 1784 and 1722 cm^{-1} at 10min. These results suggest that the amic acid structure formed by the dehydration converted to the imide structure very rapidly with elimination of water.

2-4. Conclusions

Highly crystalline particles of aromatic polyimides were obtained by the solid state polymerization of salt monomers. The morphology of the polyimide particles was quite clear and they were lozenge-shaped crystals, long plate-like crystals, fibrillar crystals and spherical aggregate of plate-like crystals. The morphology and the size of them were almost the same as those of the crystals of the corresponding salt monomers. The size and the morphologies of polyimide particles were controlled by the preparation condition of the salt monomers or chemical structure of them. The solid-state polymerization of the salt monomers proceeded with maintaining the morphology to afford high molecular weight polyimide particles. Molecular orientation in the lozenge-shaped crystal of PI(PMA/PPDA)-1 was examined and the polymer molecules aligned perpendicular to the plate-plane which was the direction of the thickness. Obtained particles possessed good thermal stability. Water and alcohol were only used as the solvent to prepare monomer salts, and hence, this procedure was environmentally benign to prepare polyimide particles.

2-5. Refrences

1. M. M. Unterlass, F. Emmerling, M. Autonietti, J. Weber, *Chem. Comm.* **50**, 430, 2014
2. M. M. Unterlass, D. Kopetzki, M. Autonietti, J. Weber, *Polym. Chem.* **2**, 1744, 2011
3. A. E. Nielsen, *Krist. Techn.* **4**, 17, 1969
4. C. A. Pride, *J. Polym. Sci., Part A; Polym. Chem.* **31**, 1045, 1993
5. K. Tashiro, M. Kobayashi, *Sen'i Gakkaishi*, **43**, 78, 1987
6. Y. Baklagina, I. S. Milevskaya, N. V. Yefanova, A. V. Sidrovich, V. A. Zubkov, *Vysokomol. Soyed.* **A18**, 1235, 1976
7. J. Liu, S. Z. D. Cheng, F. W. Harris, *Macromolecules*, **27**, 989, 1994
8. M. Ree, K. J. Chen, D. P. Kirby, *J. Appl. Phys.* **72**, 2014, 1992
9. K. Wakabayashi, T. Uchida, S. Yamazaki, K. Kimura, K. Shimamura, *Macromolecules*, **40**, 239, 2007
10. K. Shimamura, J. R. Minter, E. L. Thomas, *J. Mater. Sci. Let.* **2**, 54, 1983
11. W. W. Adams, S. Kumar, D. C. Martin, K. Shimamura, *Polym. Commun.* **30**, 285, 1989
12. K. Shimamura, T. Uchida, *J. Macromol. Sci. Phys.* **B39**, 667, 2000
13. A. Peterlin, K. Sakaoku, *Macromol. Chem.* **108**, 234, 1967

CHAPTER 3

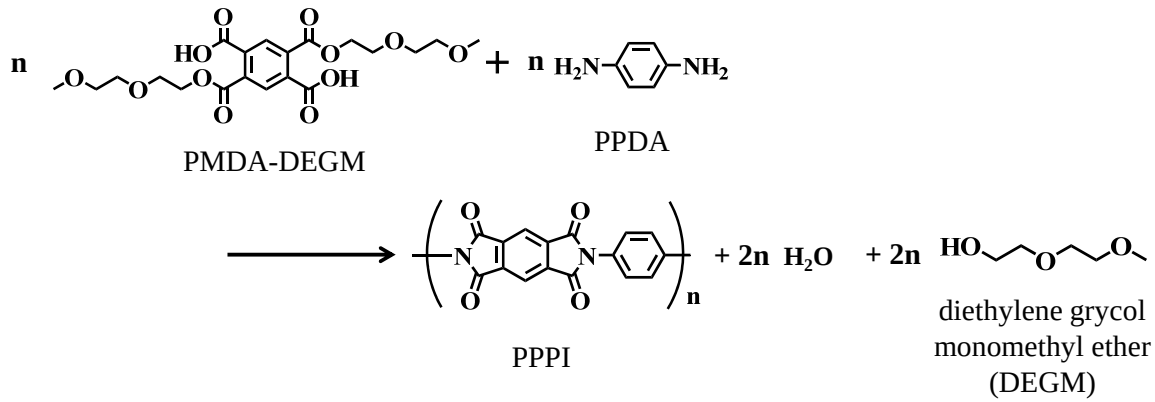
Morphology Control of Aromatic Polyimide Particles by Using Reaction-Induced Crystallization during Aqueous Solution Polymerization

3-1. Introduction

Morphology control of aromatic polyimide particles has been gathering attention to use them as higher functional fillers, and furthermore environmentally benign processing of them have been eagerly required from the view point of green chemistry. In Chapter 2, lozenge-shaped crystals of PPPI possessed high crystallinity were prepared by polymerization of salt monomers derived from PMA and PPDA. This method is very interesting in terms of using water as solvent. However, two-step procedure was required. Additionally the crystal structure of radial direction was disordered by the large conformational change due to the elimination of water from the crystals. Therefore, another approach to control the morphology in water was required. As another approach, reaction-induced phase separation during solution polymerization method was considered as a strong candidate to be able to control the higher-order structures in water as described in Chapter 1. If the polymerization combining reaction-induced crystallization will work in water, a novel environmentally benign one-step procedure will be provided for the morphology control method of aromatic polyimides particles.

In this chapter, the morphology control of PPPI crystals by using reaction-induced crystallization of oligomers during aqueous solution polymerization was examined. When PMA is dissolved in water with PPDA, salt monomers composed of them immediately precipitate as described in Chapter 2. In

order to induce crystallization of oligomers during polymerization in water, PMA was needed to be chemically modified in order to dissolve in water and not to form precipitates of salt monomers. Therefore, 2,5-Bis((2-(2-methoxyethoxy) ethoxy)carbonyl)terephthalic acid (PMDA-DEGM) which was dissolved in water was synthesized and used as monomer, and polymerization was carried out as shown in Scheme 3-1.



Scheme 3-1 Synthesis of PPPI from PMDA-DEGM and PPDA

3-2. Experimental

3-2-1. Materials

PMDA, PPDA and DEGM were purchased from TCI Co. Ltd.

3-2-2. Synthesis of PMDA-DEGM

PMDA (60.0g, 0.275mol), DEGM (72.7g, 0.605mol) and 40ml of THF were placed into a round bottle flask equipped with a reflux condenser and a thermometer. The mixture was refluxed for 24h, and then THF was evaporated. A mixture of solids and viscous liquids was obtained, washed 3 times with 300ml of

distilled water, and dried under vacuum. White crystals of PMDA-DEGM were obtained with the yield of 42.1%. ^{1}H-NMR (400MHz, DMSO-d_6, δ): 8.01(s, 2H , Ar ***H***), 4.38(t, 4H, J=4.6Hz -C***H₂***-CH_2-O-CH_2-CH_2-O-CH_3), 3.71(t, 4H, J=4.6Hz, -CH_2-C***H₂***-O-CH_2-CH_2-O-CH_3), 3.56(t, 4H, J=4.8Hz, -CH_2-CH_2-O-C***H₂***-CH_2-O-CH_3), 3.44(t, 4H, J=4.6Hz, -CH_2-CH_2-O-CH_2-C***H₂***-O-CH_3), 3.22 (s, 6H, -O-C***H₃***) ; ^{13}C-NMR (100MHz, $CDCl_3$, δ) 168.2, 165.9, 135.8, 133.2, 129.7, 72.2, 69.4, 68.6, 65.1; IR(cm^{-1}): 2907(w), 1722(s), 1494(m), 1456(m), 1236(s), 1131(s), 1113(s), 1089(s), 1075(s), 1028(m), 835(m), 756(m), 657(w); Anal. calcd. for $C_{20}H_{26}O_{12}$ (%): C 52.40, H 5.72, N 41.88; found: C 52.43, H 5.47, N 42.10.

3-2-3. Polymerization

Polymerization at 280°C was described as a typical example as follows; PMDA-DEGM (1.03g, 2.25mmol), PPDA (0.243g, 2.25mmol) and 15ml of distilled water were placed into a round bottle flask equipped with a condenser and a thermometer, and argon purged to removing oxygen. The mixture was heated at 80°C for 5 min under argon flow to dissolve the monomers. This solution (10 ml) was placed in a stainless steel cylindrical vessel (outer diameter: 12.7mm, inner diameter: 10.2mm, length: 200mm, volume: 16.4ml) under argon flow, and polymerization was carried out as shown in Figure 3-1. The vessel was sealed with a Swagelok cap, and heated at 280°C for 10 min. The reaction vessel was allowed to cool to 25°C within 2 min. Precipitated PPPI crystals were collected by filtration, washed with acetone to remove oligomers deposited on the precipitates during cooling and dried under vacuum. PPPI crystals were obtained with the yield of 95.5%. The compounds dissolving in water were recovered by freeze-drying.

Polymerizations at 210-280°C were carried out in the similar manner. Solution volume placed in the stainless steel vessel was calculated from density at

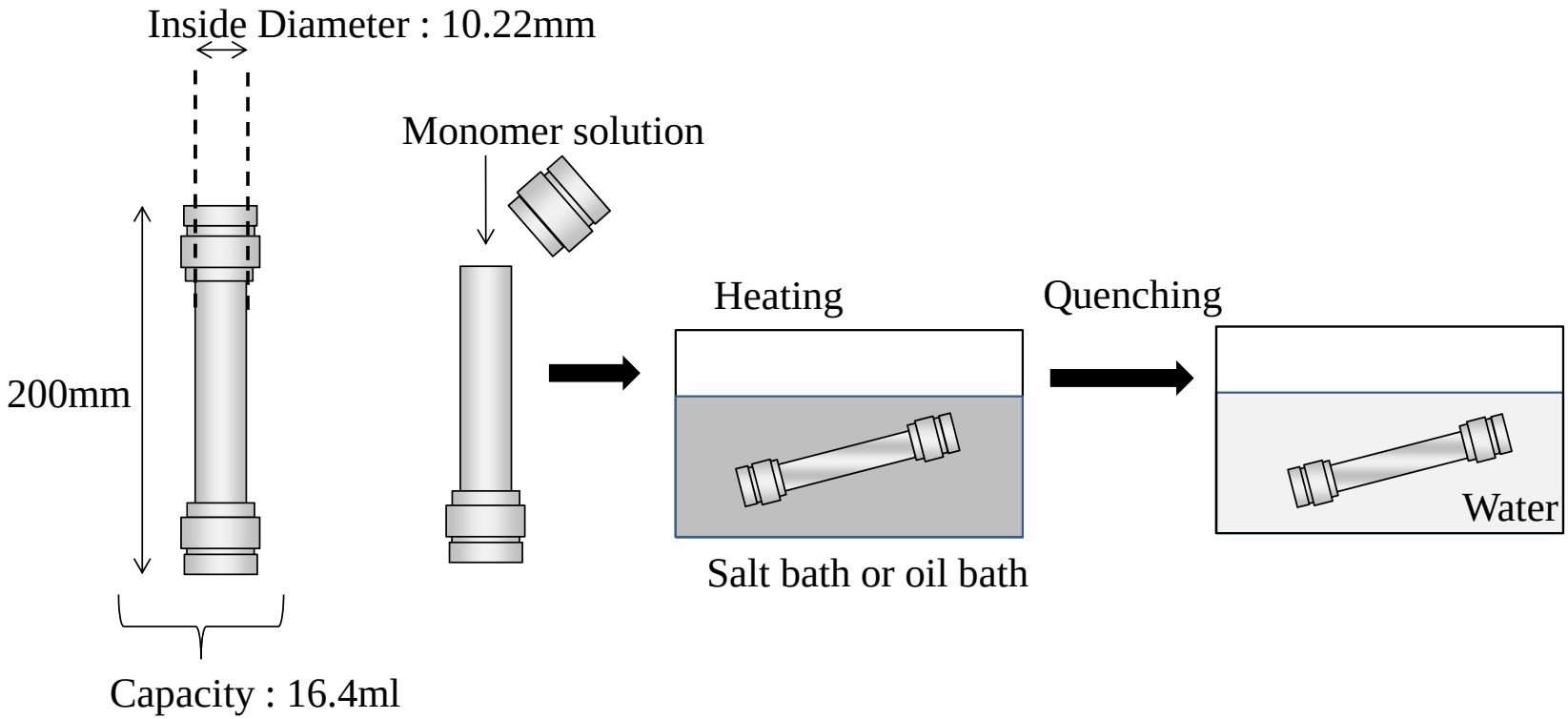


Figure 3-1 Polymerization vessel and experimental scheme

the polymerization temperature [1)] to avoid the rupture of the vessel. Polymerizations at 80°C were carried out in a round flask equipped with a reflux condenser and a thermometer.

3-2-4. Measurements

Morphology of products was observed on a HITACHI SU-3500 scanning electron microscope (SEM). Samples for SEM were sputtered with aurum and observed at 5kV. Selected area electron diffraction (SAED) was observed on a JEOL JEM2100F transmission electron microscope (TEM) at 200kV. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL JNM-ECA400 at 400MHz and 100MHz, respectively. Gel permeation chromatography (GPC) was performed on a GL Sciences GL equipped with a Shodex KF80 column and a GL Sciences GL-7450 UV detector set at 254 nm. The eluent was THF. FT-IR spectra were recorded on a Nicolet MAGNA-IR760 spectrometer. Powder patterns of wide angle X-ray scattering (WAXS) were recorded on a RIGAKU MiniFlex diffractometer with nickel-filtered CuKα radiation at 30 kV and 15 mA with a scanning rate of 1 degree/min. Thermogravimetric analysis (TG) was performed on a RIGAKU Thermo plus TGS8120 with a heating rate of 10°C/min in N_2. Atomic force microscopy (AFM) was performed on a SII SPM3800N in air.

3-3. Results and discussion

Polymerizations were carried out at 210-280°C in water at a concentration of 0.15mol/L for 3h. Pyromellitic acid (PMA) was dissolved in water and immediately formed nylon-type salts with PPDA to precipitate as described before. Therefore, PMDA-DEGM which was dissolved in water was synthesized and used as monomer. When PMDA-DEGM and PPDA were mixed in water, nylon-type

salts were not precipitated and the polymerization started in the homogeneous aqueous solution. After the polymerization for 3 h, pale yellow PPPI particles were obtained as precipitates with the yields of 88-93% as presented in Table 1. The degree of imidization (DI) calculated by FT-IR spectra was in the range of 0.7-1.0, and it increased slightly with polymerization temperature owing to the acceleration of the cyclization of amic acid moiety. [2, 3)] The PPPI precipitates prepared at 280°C hardly contained amic acid moiety, and fully cyclized PPPI was successfully synthesized in one-pot procedure. Further, both crystallite size calculated by Scherrer's equation using 110 reflection and the temperature of 5wt% loss (Td_5) measured on a TG in N_2 increased with polymerization temperature as also shown in Table 3-1. These results reveal that higher 5wt% loss (Td_5) measured on a TG in N_2 increased with polymerization temperature as also shown in Table 3-1. These results reveal that higher polymerization temperature is preferable to prepare the high crystalline and thermally stable PPPI particles. With respect to the yield, the yield at 280°C was lower than those prepared at 210 and 230°C. It is well known that aromatic polyimides are susceptible to hydrolysis in subcritical water, [4)] and hence the lower yield at 280°C might be attributed to the hydrolysis or decomposition. The polymerization time of 3 h might be slightly longer at 280°C. The polymerizations were next carried out at 280°C for 1min and 10 min. As presented in Table 3-1, the yield at 280°C for 1 min was 79.5% and that for 10 min was 95.5% which was higher than that for 3 h. Td_5 of PPPI obtained at 1min was 453°C and it was much lower even though the DI value was 0.9. In contrast to this, that for 10 min was 607°C which was the highest and crystallite size was almost the same as that prepared for 3 h. These results implied that the polymerization at 280°C for 10 min was the most suitable to afford high

Table 3-1 Results of polymerization [a)]

Run No.	Polymerization condition			Yield of precipitates [c)] (%)	DI [d)]	Td_5 [e)] (wt%)	Crystallite size [f)] (nm)
	Temp. (^oC)	Pressure [b)] (MPa)	Time				
1	210	1.9	3h	93.1	0.7	533	12.4
2	230	2.8	3h	91.2	0.8	580	14.3
3	280	6.4	3h	87.8	1.0	593	17.0
4	280	6.4	1min	79.5	0.9	453	- [g)]
5	280	6.4	10min	95.5	0.9	607	16.9
6	80	0.1	3h	1.6	0.4	- [g)]	- [g)]
7	80	0.1	24h	72.0	0.8	288	- [g)]

a) Polymerizations were carried out at a concentration of 0.15mol/L in water b) Steam pressure at polymerization temperature c) Yield of polymer precipitates based on theoretical polymer yield d) Degree of imidization calculated by FT-IR spectra e) 5 wt% loss temperature measured on a TG with a heating rate of 10^oC/min in N_2 f) calculated by Scherrer's equation using 110 reflection g) not measured

performance PPPI particles. FT-IR spectrum of the PPPI particles prepared at 280^oC for 10 min was shown in Figure 3-1 (a). The imide C=O and C-N stretching bands were clearly observed at 1784, 1722 and 1380cm^{-1}, respectively. The bands of end-groups such as amino, carboxyl, ester and anhydride groups were not visualized. This spectrum was totally identical with that of high molecular PPPI. Diffraction peaks of WAXS intensity profile were very sharp and diffuse halo caused by amorphous part could not be detected as shown in Figure 3-1 (b),

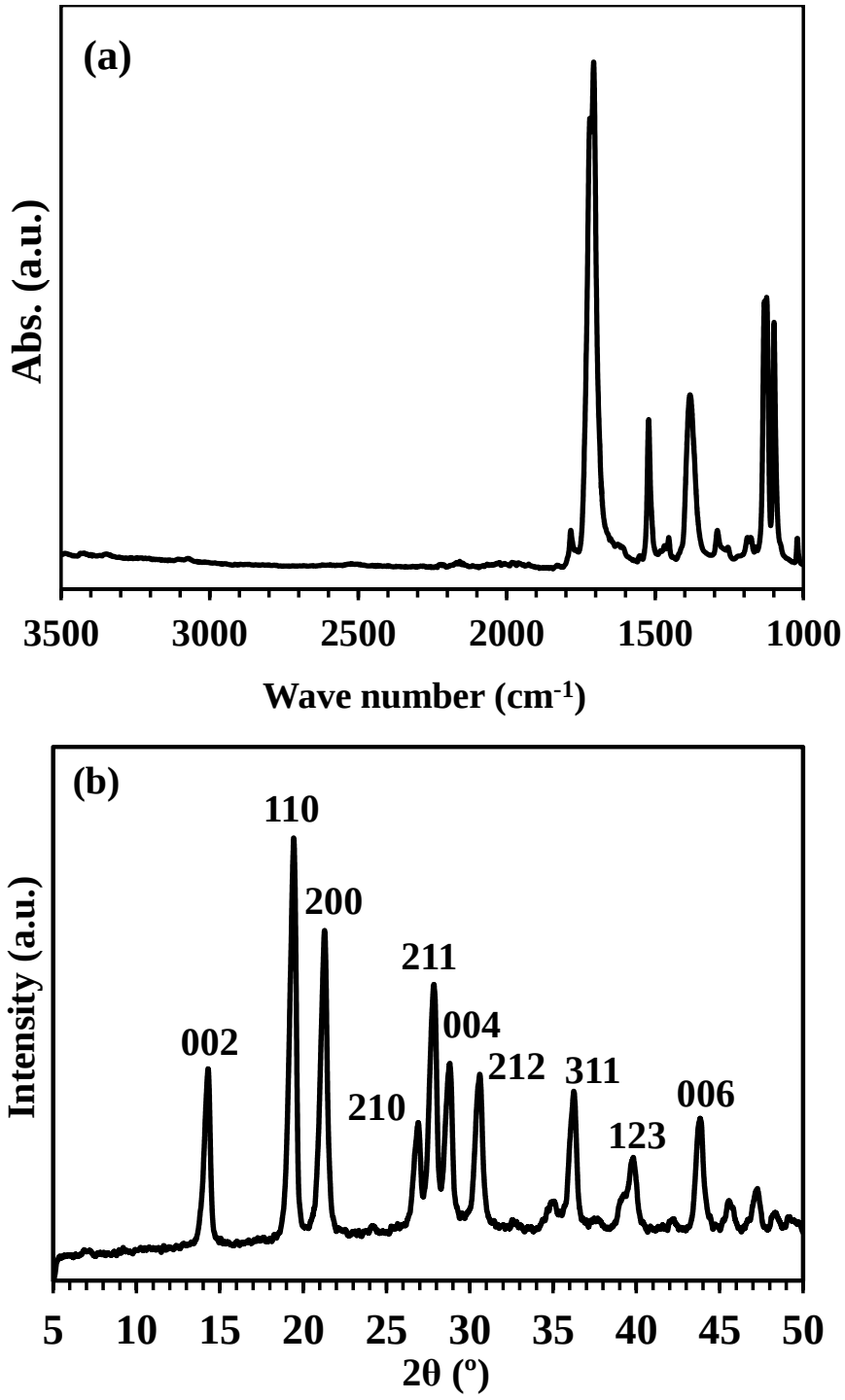


Figure 3-1 Characterization of PPPI crystals prepared at 280^{o}C for 10 min (Run No. 5). (a) FT-IR spectrum and (b) WAXS intensity profile

suggesting that the PPPI particles possessed quite high crystalinity. All diffraction peaks could be assignable by the orthorhominbic unit cell of PPPI previously reported. [5, 6)] With respect to the morphology, the PPPI particles prepared at 280°C for 10 min were plate-like crystals as shown in Figure 3-2 (a), and the thickness of them was 45-60 nm measured by an AFM as shown in Figure 3-3. In order to investigate the molecular orientation in the crystal, a selected-area electron diffraction (SAED) was taken by the irradiation of electron beam perpendicular to the plate-plane as shown in Figure 3-4. Many sharp spots were clearly observed from lower to higher-ordered diffractions, and they could be indexed. The

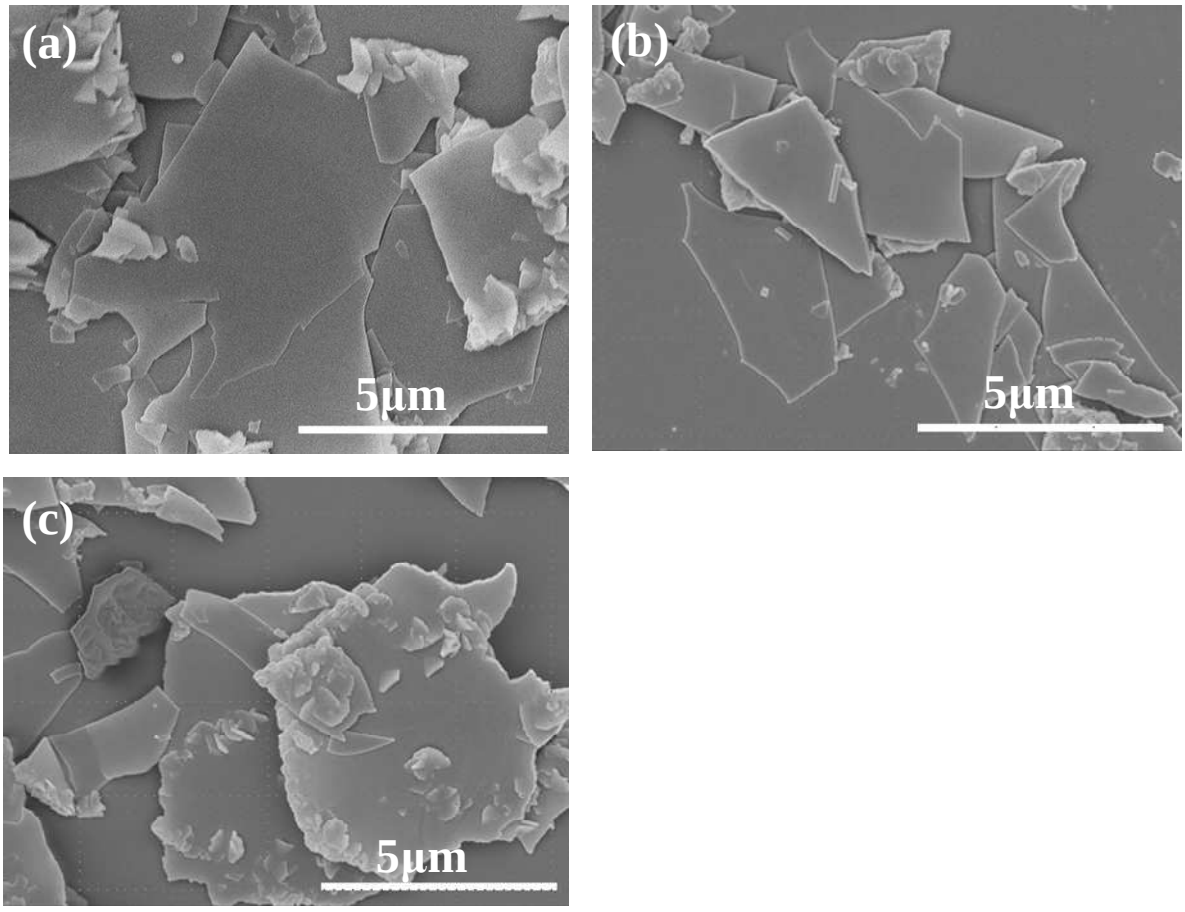


Figure 3-2 Morphology of PPPI crystals prepared at (a) 280°C for 10 min (Run No. 5), (b) 210°C for 3h (Run No.1) and (c) 230°C for 3h (Run No.3).

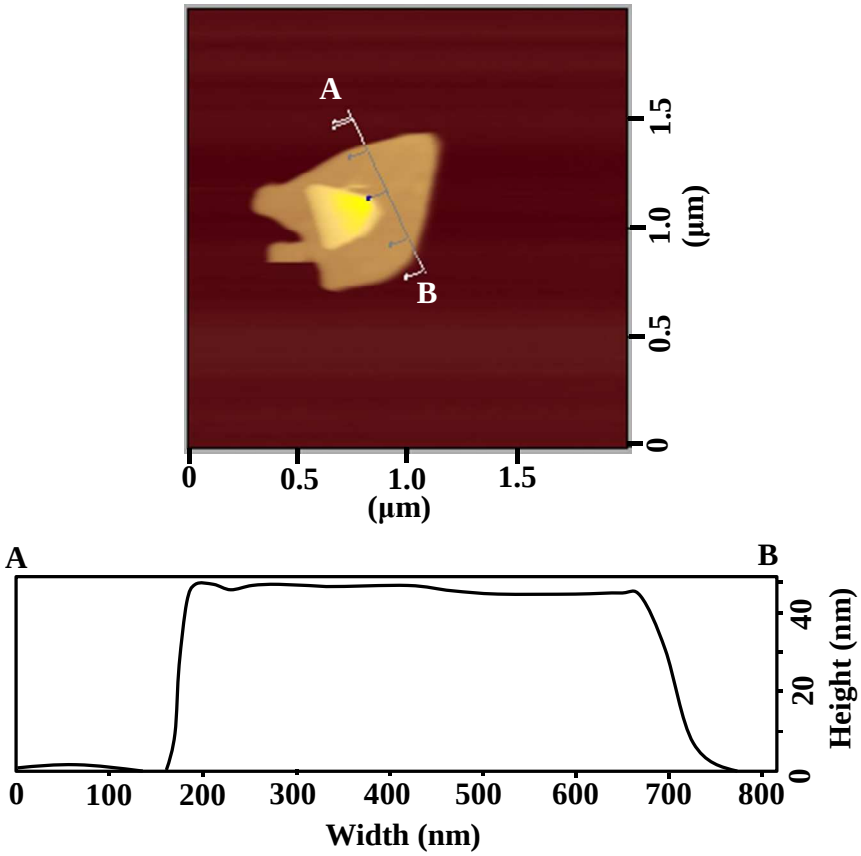


Figure 3-3 AFM image of PPPI crystals prepared at 280°C for 10 min (Run No. 5)

observed diffraction pattern indicated that the PPPI molecules aligned perpendicular to the plate-plane, corresponding to the direction of the thickness. The morphology of PPPI particles prepared at 210 and 230°C were also the plate-like as well as that of PPPI particles prepared at 280°C as shown in Figure 3-2. In order to clarify the occurrence of the reaction-induced crystallization, it needed to examine the details of the polymerization behavior, especially in the beginning of the polymerization. However, the polymerization occurred very rapidly at 280°C, and additionally the solution was allowed to cool to reduce pressure for the collection of the precipitated crystals. Oligomers dissolved in the solution at 280°C might be precipitated during cooling, especially in the beginning

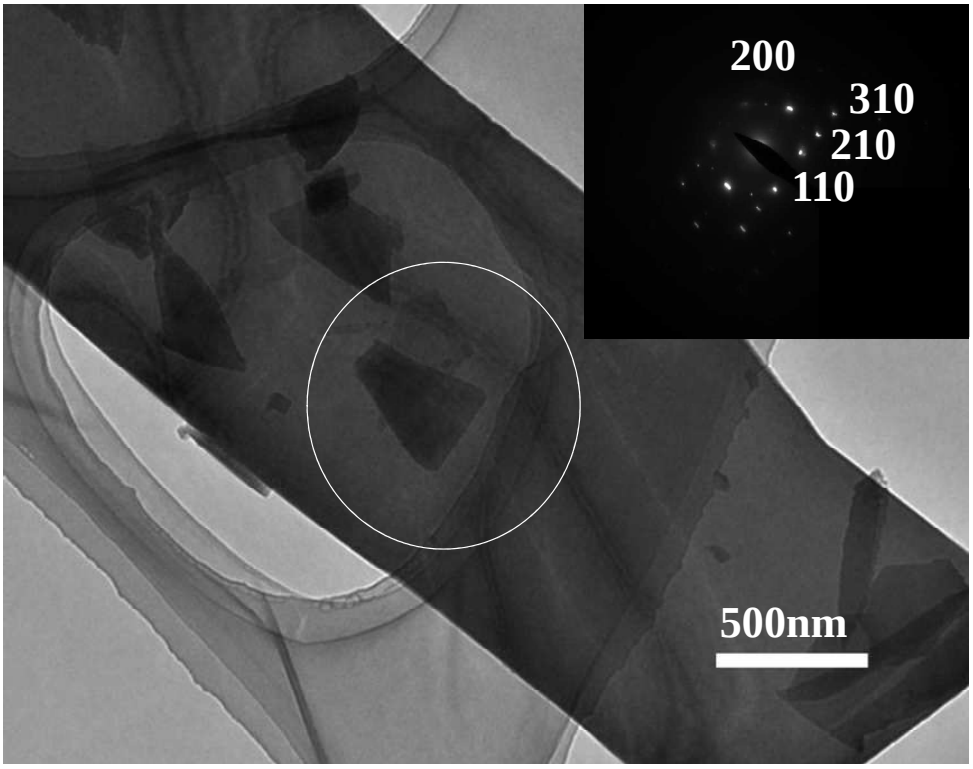


Figure 3-4 TEM image with SAED pattern of PPPI crystals prepared at 280°C for 10 min (Run No. 5).

of the polymerization. This precipitation should be avoided for the precise analysis. Because of these, lower temperature was desirable to follow the polymerization and the polymerization was carried out at 80°C for 3h and 24h. The polymerization occurred more slowly at 80°C. PMDA-DEGM and PPDA were dissolved in water to form homogeneous aqueous solution at 80°C. Then the solution became turbid after 40min by precipitation and yellow crystals were formed with time as shown in Figure 3-5 (a). Polymerization results and FT-IR spectra of the obtained particles were shown in Table 3-1 and Figure 3-5 (b), respectively. The yield and the DI value increased with time, and they were 72.0% and 0.8 after 24h, respectively. The imidization occurred even at 80°C. From the

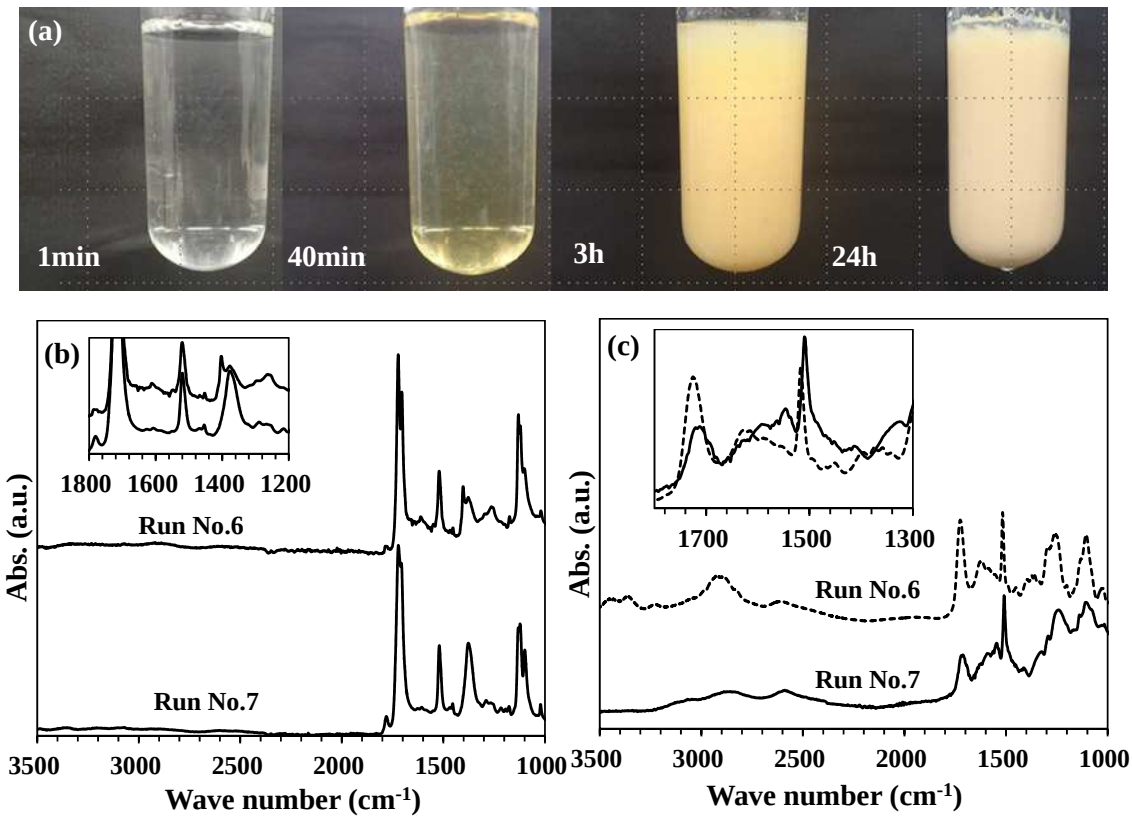


Figure 3-5 Change in features of polymerization at 80°C (a), and FT-IR spectra of (b) PPPI particles prepared at 80°C for 3 h (Run No. 6) and 24 h (Run No. 7), and (c) compounds recovered from water after polymerization at 80ºC for 3 h (Run No. 6) and 24 h (Run No. 7).

FT-IR spectrum, intensity of the band attributed to the imide C=O stretching at 1784 cm^{-1} and the imide C-N stretching at 1380cm^{-1} increased with time, being identical with the increase in the DI value. Intensity of the bands attributed to ester C-O stretching at 1260 cm^{-1} decreased with time relatively, and those attributed to amide at 1650-1690 cm^{-1} (C=O stretching) and 1550-1600 cm^{-1} (C-Nand N-H stretching) were also slightly detected. [7] These results suggest that the precipitated particles were not comprised of nylon-type salts, and they consisted of oligomers contained ester, amic acid and imide moiety. The

polymerization of oligomers proceeded in the precipitated crystals. Compounds dissolved in water were recovered after polymerization, and they were analyzed by FT-IR as shown in Figure 3-5 (c). In the early stage of polymerization, the main characteristic bands of FT-IR spectrum were identical with those of monomers, even though the bands of the amide linkage were slightly observed, owing to the slow polymerization. After 24 h, compounds recovered from water were not monomers and they contained oligomers. The bands attributed to the imide C=O stretching at 1784 cm^{-1} and the imide C-N stretching at 1380cm^{-1} were hardly detected. The band at 1725cm^{-1} assignable to ester C=O stretch became weaker with time. On the other hand, the intensity of the bands of the amide linkage increased relatively. GPC measurement was performed and the chromatograms were shown in Figure 3-6. The molecular weights of oligomers were estimated by the GPC profiles calibrated with the polystyrene standard. As known, the calculation of molecular weight was not good for the low molecular weight

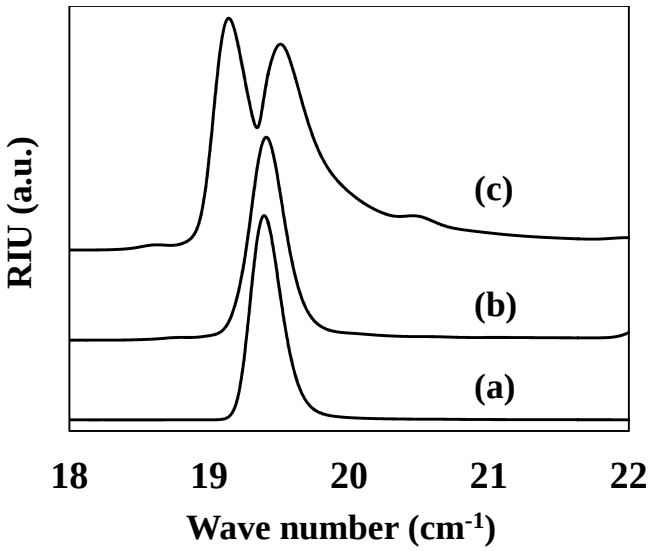


Figure 3-6 GPC chromatograms of (a) PMDA-DEGM, compunds recovered from water of (b) Run No.6 and (c) Run No.7.

compounds especially rigid molecules, and the calculated values did not show the true values. The oligomers left in water were estimated in keeping with the above. After 3h, the peak might correspond to the mixture of PMDA-DEGM and the oligo(amic acid) of one to one reactant of PMDA-DEGM and PPDA. After 24h, the main two peaks might correspond to the oligo(amic acid)s which were two to one, and one to two reactant of PMDA-DEGM and PPDA. These results clearly reveal that oligomers were formed in aqueous solution by amide-ester exchange reaction. Based on these results, the formation mechanism of the PPPI plate-like crystals could be considered as follows; In the beginning of the polymerization, oligomers were formed by the amide-ester exchange reaction in aqueous solution. When the molecular weight of oligomer exceeded a critical value, the oligomers were precipitated *via* the crystallization to form the crystals, in which the oligomer molecules oriented perpendicular to the plate-plane. Finally, the polymerization occurred in the crystals, resulting in the formation of the PPPI plate-like crystals.

3-4. Conclusion

Highly crystalline PPPI plate-like crystals were obtained in water at 280ºC only for 10 min by polymerization of water soluble PMDA-DEGM and PPDA. Additionally, molecular chains of obtained PPPI particles were aligned the thickness direction of plate-like crystals.

In order to clarify occurrence of the reaction-induced crystallization of oligomers, detailed of polymerization behavior at 80°C was investigated. As a result, in the beginning of the polymerization, oligomers were formed by the amide-ester exchange reaction in aqueous solution. Therefore, above high crystalline PPPI plate-like crystal was definitely prepared by not via precipitation of salt monomers and subsequent SSP in the crystal but reaction-induced

crystallization during aqueous solution polymerization.

This result provided a new environmentally benign procedure for the preparation of aromatic polyimide particles.

3-5. References

1. A. H. Harvey, *NIST/ASME STEAM PROPERTIES DATABASEE: VERSION 3.0; National Institute of Standards and Technology (NIST)*, 1998
2. C. A. Pride, *J. Polym. Sci., Part A; Polym. Chem.* **31**, 1045, 1993
3. Y. Seo, S. M. Lee, D. Y. Kim, K. U. Kim, *Macromolecules*, **30**, 3747, 1997
4. R. Deiasi, J. Russell, *J. Appl. Polym. Sci.* **15**, 2965, 1971
5. K. Tashiro, M. Kobayashi, *Sen'i Gakkaishi*, **43**, 78, 1987
6. Y. G. Baklagina, I. S. Milevskaya, N. V. Yefanova, A. V. Sidorovich, V. A. Zubkov, *Vysokomol Soyed*, **A18**, 1235, 1976
7. J. Kong, S. Yu, *Acta. Biochim. Biophys.* Sim. **39**, 549, 2007

CONCLUDING REMARKS

Aromatic polyimide particles have outstanding properties such as high thermal stability, mechanical property and chemical resistance, and hence they have been used for aerospace materials and electronic devices and so on. Recently, the control of higher-order structures including morphology, crystal structures and the molecular orientation has been attracted in order to obtain the essential properties predicted by their chemical structures and to use them as high functional fillers. However, it is very difficult to control the higher-order structures of aromatic polyimide particles due to their infusibility and insolubility. Environmentally benign processing of polymers has been also eagerly required from the view point of sustainable society and green chemistry. Especially utilization of “safer solvents” has been studied because large amounts of solvent were used to produce industrial materials. Then various solvents such as supercritical carbon dioxide, ionic liquids, water and alcohol have been studied as environmentally benign solvent. Although there still reminds unclear about ”what green solvents are”, water and alcohol can be considered as green solvents, because water is not only nontoxic but also nonflammable, and alcohol is environmentally benign from a life-cycle perspective.

In this thesis, two new morphology control methods for aromatic polyimide particles by using environmentally benign solvents like water and alcohol were examined. One was the combination of the preparation of salt monomers derived from aromatic tetracarboxylic acids and aromatic diamines in water and alcohol, and subsequent SSP of them. Another was the method by means of the reaction-induced crystallization of oligomers during aqueous solution polymerization.

In Chapter 1, previous studies on the morphology control of aromatic polyimide particles was surveyed to comprehend the trend of the technology and to find the possibility of the development of the environmentally benign preparation method.

Four methods to control the morphology of polyimide particles were reviewed such as the precipitation polymerization method, the re-precipitation method, the hydrothermal polymerization of salt monomers and the reaction-induced phase separation during solution polymerization method. These methods were not environmentally benign process due to usage of large amount of organic solvent except for the hydrothermal polymerization. Although the hydrothermal polymerization was very interesting in terms of the use of water as a solvent, the morphology of obtained polyimide particles was not uniform owing to the complicated heterogeneous polymerization system. With respect to the morphology control, the reaction-induced phase separation during solution polymerization method was the best way, because not only morphology but also higher-order structures was able to be tuned by various factors such as polymerization conditions and the chemical structure of using monomers and solvents. From these investigations, it was clarified that the phase separation of polymers and oligomers from homogeneous solution was important to control the morphology of them. Generally, aromatic polyimides and poly(amic acid)s are not dissolved into water and alcohol, and hence monomers which can be dissolved into them should be used to cause phase separation of formed compounds from the monomers.

Therefore, I had decided to focus on two phase separation processes through these investigations. One was crystallization of salt monomers derived from aromatic tetracarboxylic acids and aromatic diamines. Another was reaction-induced crystallization of oligomers during aqueous solution polymerization.

In Chapter 2, the preparation of four types of aromatic polyimide particles was examined by using the preparation of salt monomer crystals and subsequent SSP of them. Salt monomer crystals were obtained as precipitates by mixing of aqueous solution of PMA and BPA and aqueous solution of PPDA and ODA. The size and the morphology of the salt monomer crystals were depending on the chemical structures

and preparation condition. The morphology was quite clear and they were lozenge-shaped crystals, long plate-like crystals, fibrillar crystals and spherical aggregate of plate-like crystals. SSP of the salt monomer crystals proceeded with maintaining the morphology to afford high molecular weight polyimide particles, and hence the morphology of obtained aromatic polyimide crystals shown almost the same as the corresponding salt monomers. Molecular orientation in the lozenge-shaped crystal of PPPI was examined and it was clarified that the polymer molecules aligned perpendicular to the plate-plane which was the direction of the thickness. Obtained particles possessed good thermal stability. In this method, water and alcohol were only used as the solvent to prepare salt monomers and the polymerization was carried out in solid-state. Therefore, this procedure was confirmed as environmentally benign process to prepare highly crystalline and morphology-controlled aromatic polyimide particles.

In Chapter 3, the morphology control of PPPI crystals was examined by using reaction-induced crystallization of oligomers during aqueous solution polymerization. Highly crystalline PPPI plate-like crystals were obtained in water at 280ºC only for 10 min by the polymerization of water-soluble PMDA-DEGM and PPDA. Additionally, molecular chains were aligned the thickness direction of the PPPI plate-like crystals. In order to clarify occurrence of the reaction-induced crystallization of oligomers, details of polymerization behavior at 80^{o}C were investigated. As a result, oligomers were formed in the beginning of the polymerization by the amide-ester exchange reaction in aqueous solution. Therefore, above highly crystalline PPPI plate-like crystals were prepared by not *via* precipitation of salt monomers and subsequent SSP in the crystal, but by the reaction-induced crystallization during aqueous solution polymerization. The method using the reaction-induced phase separation during solution polymerization was known as strong candidate to control not only morphology but also higher-order structures as described in Chapter 1. Therefore, this result provided a new

environmentally benign procedure for the control of them of aromatic polyimide particles.

It is concluded that this research for the doctoral dissertation has afforded the facile and useful method for morphology control of aromatic polyimide particles by using only water and alcohol as solvents. Especially, reaction-induced phase separation during aqueous solution polymerization method is expected for an excellent environmentally benign procedure to control not only the morphology of aromatic polyimide particles but also higher-order structures of them. These results have to contribute significantly to acceleration of application of the polyimide materials as high performance fillers and carbon precursors, and these methods give an answer to solve the environmental problems in the field of polymer synthesis.

LIST OF PUBLICATIONS

1. Hydrothermal Synthesis of Aromatic Polyimide Particles by using Reaction-Induced Crystallization

   Daisaku Shojo, Shinich Yamazaki, Kunio Kimura

   Journal of Polymer Science; Part A: Polymer Chemistry (accepted 24 July 2015, DOI: 10.1002/pola.27791)

ACKNOWLEDGEMENTS

I would like to express my heartfelt and deepest gratitude to Professor Dr. Kunio Kimura, Graduate School of Environmental and Life Science, Okayama University, for fruitful discussion, proper guidance, valuable advice, numerous helpful suggestions and cordial encouragements throughout this work. I also deeply appreciate that he gave me many precious opportunities to give a presentation in a large number of academic conferences. I also owe a very important debt to him about giving me many realizations about the importance of decision after deep deliberation.

I am deeply grateful to Professor Dr. Yukitaka Kimura, Graduate School of Environmental and Life Science, Okayama University, for his numerous helpful advices and their helpful suggestions and proper guidance.

I am deeply grateful to Associate Professor Dr. Yutaka Takaguchi, Graduate School of Environmental and Life Science, Okayama University, for his numerous helpful advices, valuable suggestions and warm encouragements throughout this study.

I am cordially grateful to Associate Professor Dr. Shinichi Yamazaki, Graduate School of Environmental and Life Science, Okayama University, for his valuable advice, numerous helpful suggestions and counsels throughout this work.

I would like to express my heartfelt and deepest gratitude to Emeritus professor Dr. Yuhiko Yamashita, Okayama University, for his many helpful advices and suggestions, proper guidance and cordial encouragements throughout this work.

I am deeply grateful to Mr. Masahiro Sato, KRI Inc., for his many helpful advices and warm encouragements. I also deeply appreciate that he gave me many precious chances to join a large number of academic conferences.

I am deeply grateful to Dr. Hidekazu Sugimori, Analysis Research Center, KRI Inc., for his numerous helpful advices, valuable suggestions, beneficial analytical supports and warm encouragements throughout this study.

I deeply thank to all members, past and present of Kimura laboratory for their cooperation and friendship throughout this study. I will never forget that I had an invaluable time with them in the Kimura laboratory.

I deeply thank to all members, of New Functional Research Laboratory, KRI Inc., for their cooperation and friendship throughout this study. I would like to return the compliment through future works in company.

And, I would like to express my heartfelt thanks to my family for warm constant assistances and encouragements through my study.

Daisaku Shojo

Graduate School of Environmental and Life Science

Okayama University

Japan

September 2015