

Morphology Control of Aromatic Polymers by means of Phase Separation of oligomers during Polymerization

Kunio Kimura

Faculty of Environmental Science and Technology, Okayama University,

3-1-1 Tsushima-naka, Okayama 700-8530 JAPAN

Tel & Fax: +81-86-251-8902, e-mail: polykim@cc.okayama-u.ac.jp

INTRODUCTION. Wholly aromatic polymers consisting of rigid-rod molecules have been receiving much attention as high performance materials because they are expected to show several excellent properties such as thermal stability, chemical resistance, high strength and so on. Numerous types of rigid-rod aromatic polymers have been synthesized so far. The synthesis and processing of these materials are generally more difficult than for conventional flexible chain polymers due to strong enthalpic interactions and the minimal increase in conformational entropy associated with dissolution or melting. Many of them exhibit neither solubility nor meltability due to the rigid structure, and hence some of them could not be used as industrial materials. The relation between high performance and processability is always trade-off and the history of the development of aromatic polymers can be regarded as the challenge to overcome this antagonistic problem. Many studies have been conducted to conquer this intractability without the drop of the properties from the aspect of chemical modifications. These chemical modifications enhance the processability of some rigid-rod polymers. However, chemical modification of polymer backbone usually shorten the rigidity leading to the reduction of their essential properties.

Poly(*p*-phenylene pyromelliteimide) (PPPI) has been receiving much attention [1-3] because

of the predicted outstanding properties, especially the highest modulus over 500GPa [4]. PPPI exhibits infusibility and this makes it inaccessible for processing by conventional techniques. PPPI has been usually prepared by a two-step procedure including the synthesis of a soluble poly(amic acid) precursor and the following imidization [5,6]. The difficulty of the orientation of poly(amic acid) precursor and the rapid crystallization during imidization prevent to control the morphology of PPPI.

It has been known that needle-like polymer crystals consisted of fully-extended molecular chains possess the most desirable morphology to withdraw the essential properties of polymer, but it is usually very difficult to prepare the fully-extended polymer chain crystal. We have been studying the morphology control of wholly aromatic polyesters by means of oligomer crystallization during solution polymerization, and the whiskers and microspheres of aromatic polyesters were successfully prepared by polymerization of the corresponding acetyl carboxylic acid in liquid paraffin [7-14]. Figure 1 shows poly(*p*-oxybenzoyl) (POB) whiskers and poly(*p*-oxycinnamoyl) (POC) microspheres. These whiskers and microspheres are formed by crystallization and liquid-liquid phase of oligomers, respectively. These studies reveal that the self-assembling polymerization by means of the reaction-induced crystallization of oligomers is a valuable method for the

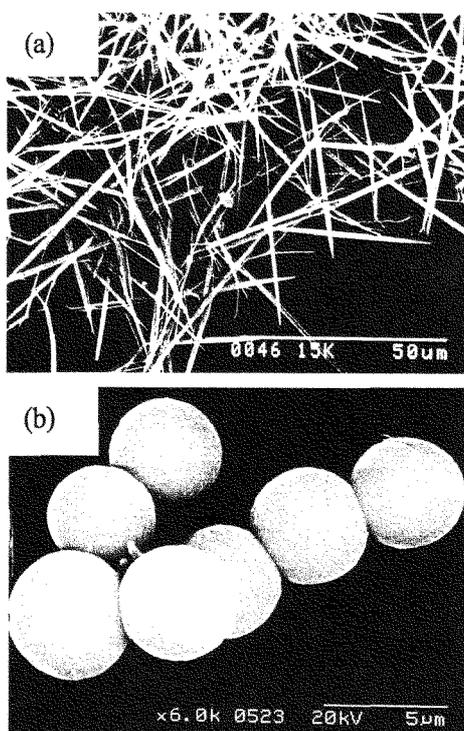


Figure 1. (a) POB whiskers and (b) POC microspheres

morphology control of intractable polymers and morphology of PPPI can be also controlled by this method.

This paper describes the results of our new finding on the morphology control of PPPI by means of the phase separation of oligomers during the solution polymerization of *p*-phenylene diamine (PPDA) and pyromellitic dianhydride (PMDA).

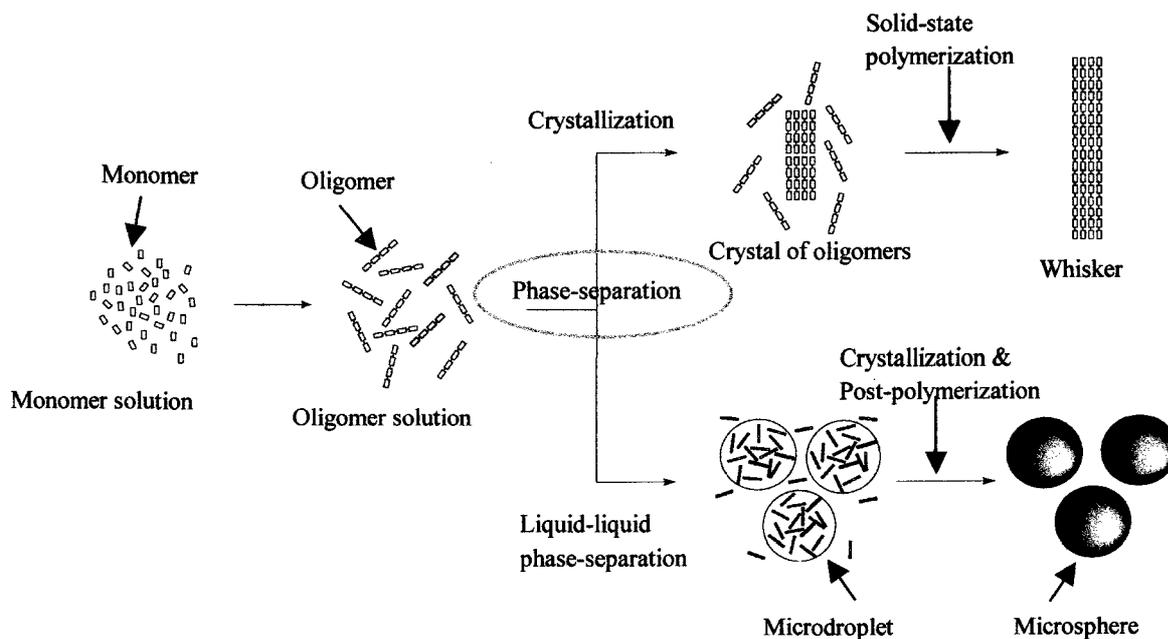
EXPERIMENTAL. A typical run was described as follows (Run No. 2 in Table 1). Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube were placed PMDA (0.075 g, 0.34 mmol), which was purchased from Aldrich Co. Ltd. and recrystallized from acetic anhydride, and 20 mL of liquid paraffin. The reaction mixture was heated under a slow stream of nitrogen up to 330°C with stirring. When PMDA was completely dissolved on heating, PPDA (0.037 g,

0.34 mmol), which was a gift of Taishin Kasei Kogyo Co. Ltd. and used as received, was added at 280°C into the solution. PPDA was completely dissolved within 1 minute under stirring, and then the stirring was stopped. The solution became turbid within 30 seconds due to the precipitation of oligomers. The temperature was maintained at 330°C for 6 hours. The precipitated products were collected by vacuum filtration at 330°C, and washed with *n*-hexane and acetone. The filtrate was poured into *n*-hexane, and the precipitated oligomers which were dissolved in liquid paraffin at 330°C were collected by filtration. IR of the polymer products (KBr) (cm^{-1}): 1784, 1721, 1520, 1454, 1376, 1187, 1131, 1098, 1021, 918, 854, 809, 722, 646, 529. IR of the recovered oligomers (KBr) (cm^{-1}): 3391, 3150-2600, 3056, 2924, 2854, 1854, 1781, 1724, 1605, 1515, 1381, 1317, 1253, 1203, 181, 1132, 1017, 904, 805, 720, 699, 618, 529.

RESULTS AND DISCUSSION.

General principle of morphology control

Basic concept of the former method is shown in Scheme 1. In this method, the solvents which are miscible to monomers and immiscible to polymers are needed to induce the phase-separation of oligomers. The oligomers are formed by the reaction in solution phase. The physical properties of oligomers such as solubility, crystallizability, freezing temperature, crystallinity and so on are highly related to the molecular weight. When the molecular weight of oligomers exceeds the critical value, they are phase-separated through the super-saturated state. There are two modes for the phase-separation of oligomers, which are crystallization and liquid-liquid phase-separation. If the oligomers are phase-separated by the crystallization,

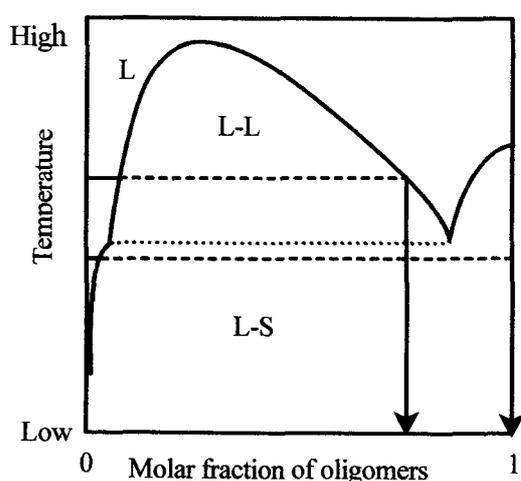


Scheme 1. Concept for morphology control by means of phase separation of oligomer during solution polymerization.

oligomer crystals are formed. The solid-state polymerization occurs very efficiently, and finally the polymer crystals such as whisker are obtained. On the other hand, if they are phase-separated through liquid-liquid phase separation, the microdroplets of concentrated phase are formed in the solution. The further polymerization occurs in the microdroplets due to the higher concentration of oligomers and then it results in the solidification of microdroplets with maintaining the spherical morphology. The microspheres are eventually obtained. The behavior of phase separation of oligomers determines the morphology, which is governed by the miscibility between the oligomer and the solvent. The phase separation diagram can be schematically illustrated in Scheme 2, which is the analogous concentration-temperature (C - T) phase diagram to that of partially miscible polymer-solvent system [15,16]. The phase

separation curve in the repulsive system in which there is no attractive interaction between oligomer and solvent is written as the combination of the freezing point curve of oligomers and the upper critical solution temperature (UCST) type consolute curve. If the super-saturated oligomers are precipitated across the freezing point curve, they are precipitated by crystallization to form the crystals. On the other hand, if they are precipitated across the consolution curve, microspheres are formed through liquid-liquid phase separation and the following further polymerization. As aforesaid, the formation of the POB whisker and the POC microsphere are the typical examples of crystallization and liquid-liquid phase separation, respectively. From the morphological observation of the POB whiskers during polymerization, the details of the formation mechanism had been proposed. The oligomers

having the degree of polymerization of more than 8 are crystallized in the form of lamellae from solution polymerization. Next, the screw dislocation is generated in the precipitated lamellae which are nuclei and then the needle-like crystals are formed with the spiral growth. The oligomers are preferentially crystallized on the spiral step of the crystals due to the first advantage of surface energy. Finally, the post polymerization occurs topochemically between oligomers in the interlamellar regions of the crystals. This solid-state polymerization proceeds very effectively to result in the very high molecular weight polymers of which number average degree of polymerization reaches to 1,800 after 24 hours polymerization because the oligomer chain end groups are in good position to polymerize in the crystals. On the other hand, the formation mechanism of the POC microspheres has also been proposed. The POC microspheres are prepared by the polymerization of (*E*)-4-acetoxycinnamic acid in liquid paraffin at 330°C. This POC has C=C moiety conjugated with 1,4-phenylene moiety, and therefore the miscibility of oligomer and liquid paraffin is



Scheme 2. Schematic C-T phase diagram for partially miscible oligomers and solvent system. L: miscible liquid phase, L-L: two immiscible liquid phase, L-S: liquid and solid phase

much lower than that of POB. When the degree of polymerization of the oligomers exceeds the critical value, liquid-liquid phase-separation occurs to form the microdroplets. They are grown by not only the consecutive supply of the oligomers from the solution but also the coalescence of the microdroplets. Finally the subsequent polymerization in the microdroplets results in the formation of microspheres as described.

Several publications have been devoted to the preparation of polyimide particles [17-20]. Many of them are based on the precipitation from polymer solution by using the progressive decrease of solubility of rigid poly(aromatic amic acid) precursor in an aprotic polar solvent undergoing a thermal imidization. However, the preparation of the PPPI crystal and the morphology control are not achievable by these preparative procedures. As aforesaid, the reaction-induced phase separation of oligomers during polymerization must create new morphology of PPPI such as whisker and microsphere.

Morphology control of PPPI

Polymerizations were carried out at 330°C. After the addition of PPDA, the solution became turbid immediately and the orange precipitates were obtained with the yield of over 80%. The morphology of the products is susceptible to not only the polymerization concentration but also the solvent as shown in Table 1. Figure 2 shows the morphology of the products. With respect to the polymerization in liquid paraffin, the polymerizations at the concentration of 1.00 % and 0.50 % yield the microspheres, of which the surface is slightly rough. The average diameter of the microspheres is dependent on the concentration, and that

Table 1. Results of polymerization ^a

Run No.	Polymerization condition				Yield (%)	Morphology	10 wt% loss temperature (°C) ^c
	Solvent	Conc. (%)	Time (hr)	Addition temp. ^b (°C)			
1	LPF	1.00	6	280	80.0	Spherical (D=1.05, cv=34.2 ^d)	710
2	LPF	0.50	6	280	85.0	Spherical (D=0.55, cv=41.8)	737
3	LPF	0.25	6	280	80.4	SA ^e , Lozenge-shaped	727
4	LPF	0.15	18	280	84.3	SA, Lozenge-shaped	681
5	TS10	0.50	6	240	83.8	Spherical (D=0.83, cv=39.2)	685
6	TS10	0.50	6	280	85.0	SA, Lozenge-shaped	721
7	TS10	0.50	6	330	85.1	SA, Lozenge-shaped	721

a: Polymerizations were carried out at 330°C.

b: Temperature at which PPDA was added after PMDA was completely dissolved.

c: measured on TGA with a scanning rate of 20°C·min⁻¹ in nitrogen.

d: D is the average diameter (μm) and cv is the coefficient of variation (%) of the microspheres.

e: SA stands for the star-like aggregates of needle crystals.

prepared at the concentration of 1.00 and 0.50 % are 1.05 μm and 0.55 μm, respectively. The higher concentration gives the longer diameter. These microspheres exhibit broader distribution of the diameter. In contrast to this, the

morphology of the products is drastically changed when the polymerization is carried out at the lower concentration than 0.50%. The star-like aggregates of needle crystals and the lozenge-shaped crystals are formed. The large

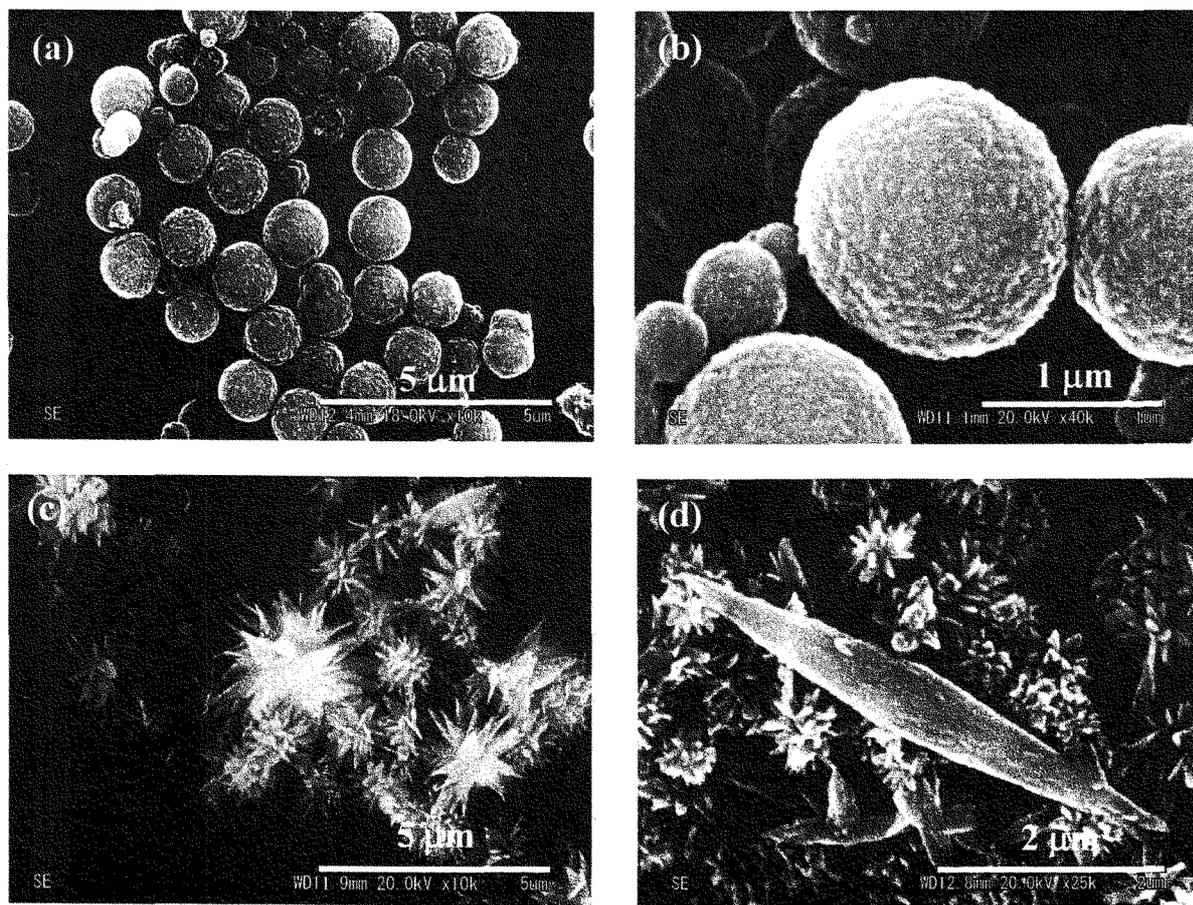


Figure 2. Morphology of PPPI. Micrographs of (a) and (b) are the microspheres of Run No. 1. Those of (c) and (d) are the star-like aggregates of needle crystals and the lozenge-shaped crystals of Run No. 7.

lozenge-shaped crystal is found in the product prepared at the concentration of 0.15%, of which the length of the longer diagonal line is 4.9 μm and that of the shorter line is 0.7 μm . It has been reported that the lower concentration has a tendency to induce the crystallization of oligomers because the molecular weight of the phase-separated oligomers becomes higher and this brings about the increase of the freezing point of the oligomers [21]. In the case of this study, the influence of the polymerization concentration on the morphology is consistent with the previous results and this fact suggests that the phase separation behavior of the oligomers governs the morphology of PPPI.

In order to elucidate the influence of the solvent on the morphology, polymerization was carried out in Therm S 1000 (TS10) [22] at the concentration of 0.50%. In contrast to the result in liquid paraffin, the star-like aggregates of needle crystals and the lozenge-shaped crystals are formed. The miscibility between the oligomers and TS10 is higher comparing with liquid paraffin. It has been clarified that the

higher miscibility between the oligomer and the solvent makes the two immiscible liquid phase narrow on the *C-T* phase diagram and leads to the crystallization of oligomers [23,24]. The solvent effect in the polymerization of PPPI is in agreement with the previously reported tendency. Temperature at which PPDA is added also influences the morphology. When PPDA is added at 240°C, the microspheres are formed, of which the average diameter is slightly longer than that prepared in liquid paraffin at the same concentration. The crystals are formed when PPDA is added over 280°C.

All the obtained products were totally insoluble into organic solvents, and therefore the chemical structure of the products was analyzed by FT-IR. The characteristic bands of imide group appear clearly at 1784 and 1722 cm^{-1} which are C=O stretch [25]. The band of C-N stretch appears at 1376 cm^{-1} . Furthermore, the band attributed to the deformation of the imide ring or the imide carbonyl groups also appears at 722 cm^{-1} . The bands for end groups such as amino group and anhydride group, which are observed at

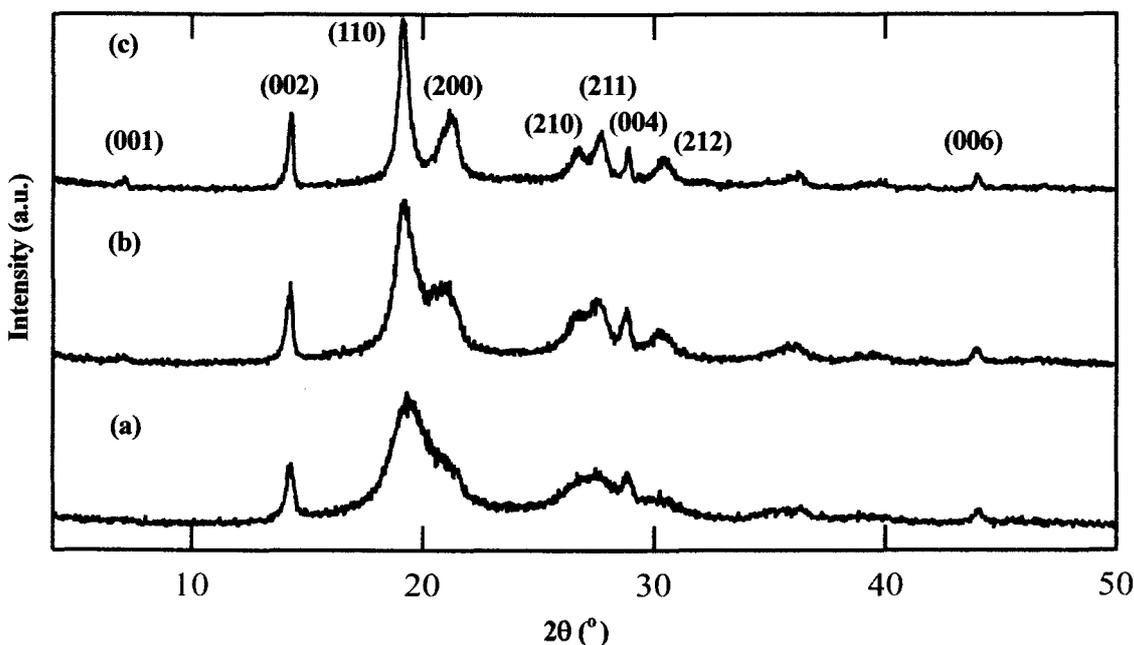


Figure 3. WAXS intensity profiles of microspheres of Run No. 5 (a), and the mixture of star-like aggregates of needle crystals and lozenge-shaped crystals of Run No. 6 (b) and No. 7 (c).

ca. 3400 cm^{-1} and 1855 cm^{-1} in the spectrum of the dissolved oligomers, are not appeared in the spectrum of the products. This spectrum is identical with that of PPPI. In the spectrum of the dissolved oligomers, the characteristic bands for imide appear from the beginning of the precipitation. Additionally, the band of N-H in amino group and / or amic acid moiety and that of anhydride are observed. The broad band of OH in carboxylic acid and that of amide linkage slightly appear at $3150 - 2600\text{ cm}^{-1}$ and 1605 cm^{-1} , respectively. These results indicate that the almost imidized oligomers contained a little amic acid moiety are formed in the solution *via* the formation of oligo(amic acid) and the subsequent thermal imidization due to the higher temperature. And then they are phase-separated through the super-saturation state to form the microspheres or the crystals. The post-polymerization occurs in the products due to the high polymerization temperature as previously reported [26], and the microspheres or the crystals of PPPI are finally obtained.

Figure 3 shows the WAXS intensity profiles of the microspheres, and the mixture of the star-like aggregates of needle crystals and the lozenge-shaped crystals. The reflection peaks are clearly observed and these products possess high crystallinity. These peaks can be described with the PPPI orthogonal unit cell [4,27]. The peaks from the mixture of the star-like aggregates of needle crystals and the lozenge-shaped crystals are shaper than those from the microspheres. In particular, the mixture of the star-like aggregates of needle crystals and the lozenge-shaped crystals prepared in TS10 by the addition at 330°C exhibit the quite sharp and well-resolved peaks, and the diffuse halo attributed to amorphous parts is scarcely observed. These products are comprised of well-organized crystal structure.

Thermal properties of the products were evaluated by thermogravimetric analysis with a scanning rate of $20^{\circ}\text{C} \cdot \text{min}^{-1}$ in nitrogen atmosphere. Thermal decomposition temperatures of 10wt% loss in nitrogen are quite high in the range of $681-737^{\circ}\text{C}$. That of PPPI prepared by a conventional procedure was reported as 632°C [28]. The PPPI products prepared in this study exhibit better thermal stability than that prepared by a conventional method due to the higher crystallinity. These products exhibit neither glass transition temperature nor melting temperature under the thermal decomposition temperature. These products are in the highest class of thermally stable polymers.

CONCLUSION. Microsphere and crystals of PPPI are prepared by the phase separation of oligomers during solution polymerization. Especially, the lozenge-shaped crystal has extremely high crystallinity. These PPPIs exhibit outstanding thermal stability and seem to possess quite high potential for high-performance materials.

REFERENCES.

- [1] Sroog, C. E. *J. Polym. Sci. Macromol. Rev.* **1976**, *11*, 161.
- [2] Bessonov, M. I., Koton, M. M., Kudryavtsev, V. V. And Laius, L. A. *Polyimides: Thermally Stable Polymers*. Consultants Bureau, New York **1987**.
- [3] Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*, Blackie, New York **1990**.
- [4] Tashiro, K.; Kobayashi, M. *Sen-i Gakkaishi* **1987**, *43*, 78.
- [5] For example: Cassidy, P. E. *Thermally Stable Polymers, Syntheses and Properties*. Marcel Dekker, New York, **1980**.
- [6] Mittal, K. L. *Polyimides, Synthesis, Characterization, and Application, Vol. 1*, Plenum Press, New York, **1984**.
- [7] Yamashita, Y.; Kimura, K. *Polymeric Materials Encyclopedia*, CRC Press **1996**, 8707.

- [8] Yamashita, Y.; Kato, Y.; Endo, S.; Kimura, K. *Makromol. Chem. Rapid Commun.* **1988**, *9* (9), 687.
- [9] Kimura, K.; Endo, S.; Kato, Y.; Yamashita, Y. *Polymer* **1994**, *35*, 123.
- [10] Kimura, K.; Endo, S.; Kato, Y.; Yamashita, Y. *Polymer*, **1993**, *34*, 1054.
- [11] Kimura, K.; Kato, Y.; Inaba, T.; Yamashita, Y. *Macromolecules* **1995**, *28*, 255.
- [12] Kimura, K.; Ohmori, H.; Yokoyama, F.; Yamashita, Y. *Polymer Preprints, Div. of Polymer Chem., ACS*, **1998**, *39*, 863.
- [13] Kimura, K.; Yamashita, Y. *The Polymer Processing Society, 14th Annual Meeting, Proceedings*, **1998**, 577.
- [14] Kimura, K.; Yamashita, Y. *Polymer* **1994**, *35*, 3311.
- [15] Richards, R. B. *Trans. Faraday Soc.* **1946**, *42*, 10.
- [16] Flory, P. J.; Mandelkern, L.; Hall, H. K. *J. Am. Chem. Soc.* **1951**, *73*, 2532.
- [17] Basset, F.; Lefrant, A.; Pascal, T.; Gallot, B.; Sillion, B. *Polym. Adv. Tech.* **1998**, *9*, 202.
- [18] Lin, T.; Stickney, K. W.; Rogers, M.; Riffle, J. S.; McGrath, J. E.; Marand, H.; Yu, T. H.; Davis, R. M. *Polymer* **1993**, *34*, 772.
- [19] Asao, K.; Ohnishi, H.; Morita, H. *Koubunshi Ronbunshu* **2000**, *57*, 271.
- [20] Nagata, Y.; Ohnishi, Y.; Hatori, H.; Shiraishi, M.; Kajiyama, T. *Polymer Preprints, Japan* **1994**, *43*, 3115.
- [21] Kimura, K.; Ohmori, H.; Yokoyama, F.; Yamashita, Y. *Polymer Preprints, Div. of Polymer Chem., ACS*, **1998**, *39*, 863.
- [22] TS10, which was a mixture of the isomers of dibenzyltoluene, was purchased from Nippon Steel Chemical Co. Ltd. and purified by vacuum distillation.
- [23] Kimura, K.; Inoue, H.; Kohama, S.; Yamashita, Y.; Sakaguchi, Y. *Macromolecules*, **2003**, *36*, 7721.
- [24] Kimura, K.; Yamashita, Y. *The 2nd International Conference on POLYCONDENSATION 1998, Proceedings*, **1998**, 124.
- [25] Pryde, C. A. *J. Polym. Sci.: Part A: Polym. Chem.* **1989**, *27*, 711.
- [26] Kumagai, Y.; Itoya, K.; Kakimoto, M.; Imai, Y. *Polymer* **1995**, *36*, 2827.
- [27] Baklagina, Y. G.; Milevskaya, I. S.; Yefanova, N. V.; Sidorovich, A. V.; Zubkov, V. A. *Vysokomol. Soyed.*, **1976**, *A18*, 1235.
- [28] Hsiao, A. H.; Chen, Y-J. *Eur. Polym. J.* **2002**, *38*, 815.