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Structural study on rodlike aromatic polyimides derived by solid-state thermal and chemical imidization of poly(amic *n*-dodecyl ester)

Katsuhiro Inomata*, Yuki Ozeki, Sachi Shimomura, Yuhji Sakamoto, Eiji Nakanishi

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

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Abstract

Para-linked aromatic poly(amic *n*-dodecyl ester) (PA-12), in which long *n*-alkyl side chains are attached on rodlike aromatic polyamide, was prepared by polycondensation of 2,5-bis(1-dodecyloxycarbonyl)terephthaloyl chloride and 1,4-diaminobenzene. In as-cast PA-12 film, formation of layered structure with alternating main-chain-segregated and side-chain-segregated layers is suggested by X-ray diffraction measurement. PA-12 is a precursor of rodlike aromatic polyimide, poly(1,4-phenylene pyromellitimide) (PPPI). Solid-state thermal imidization and base-catalyzed chemical imidization of PA-12 film has been investigated. Although the layered structure of PA-12 was destroyed during the imidization reaction, the obtained PPPI exhibited lower density than densely packed PPPI. This result may indicate that the side chain-segregated domain was transformed to a cavity surrounded by PPPI after the imidization reaction. Chemical imidization in pyridine/toluene mixture and subsequent heating at 200 °C was the optimum condition to obtain low density PPPI.

Keywords: Polyamide; Polyimide; Chemical imidization; Layered structure; Density

1. Introduction

Rodlike aromatic polyesters, polyamides, and polyimides are expected as high performance materials because of their excellent mechanical and thermal properties. Some rodlike polymers, on which flexible side chains are introduced, have been investigated for the purpose of good processability and solubility. Because of the difference in chemical structure of the aromatic main chain and aliphatic side chain, it has been reported that the main chains and side chains forms respective segregated domains [1–7]. As the result of this micro-segregation, these rodlike polymers form ordered morphology, i.e., layered structure with alternating main chain- and side chain-segregated layers.

Recently, Watanabe et al. [8,9] reported a unique mesophase in rodlike polyesters, poly(*p*-biphenylene terephthalate) with flexible alkoxy side chains on the terephthalate moiety (PBpT-O*n*). For long alkyl side chains (carbon number $n > 16$), ordinary layered mesophase was observed below the mesophase-isotropic transition temperature. On the other hand, polyesters with shorter alkyl side chains than $n = 12$ exhibited hexagonal columnar phase, in which the alkyl side chains form segregated cylindrical domain, and the strongly associated main chain are surrounding the cylindrical domain like honeycomb structure. These layered and honeycomb structures have analogy with the microphase separated structure of diblock copolymer, i.e., lamellar and cylinder structure [10,11]. In diblock copolymers, the segregation power of the consisting block chains induces the formation of segregated domains, and its morphology depends on the volume fraction of each block. When the volume fraction of the diblock copolymer is asymmetric, the minor block forms cylindrical domain and the major block surrounds the cylinder as the matrix domain. The formation of honeycomb or layered structure in rodlike polyesters with depending on the alkyl chain length can also be described by the volume fraction of main chain and side chain.

Because the size of the side-chain-segregated domain depends on the alkyl chain length, the diameter

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* Corresponding author. Tel./fax: +81 52 735 5274.
E-mail address: inomata.katsuhiro@nitech.ac.jp (K. Inomata).

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distribution of the cylinder should be sharp with nanometer order. The segregated alkyl-chain domain and matrix aromatic main chain domain have different physical properties, i.e., the former contains flexible non-polar chains and liquid-like above ~50 °C, and the latter contains rigid aromatic and polar ester group. In this sense, the surrounded cylindrical domain can be regarded as a liquid-like path in the rigid matrix, and the diameter of the path is close to low-molecular-weight substances. If the alkyl chains can be removed without any influence on the matrix domain, a unique mesoporous material [12–14] with nanometer-sized voids or cavities will be possibly prepared.

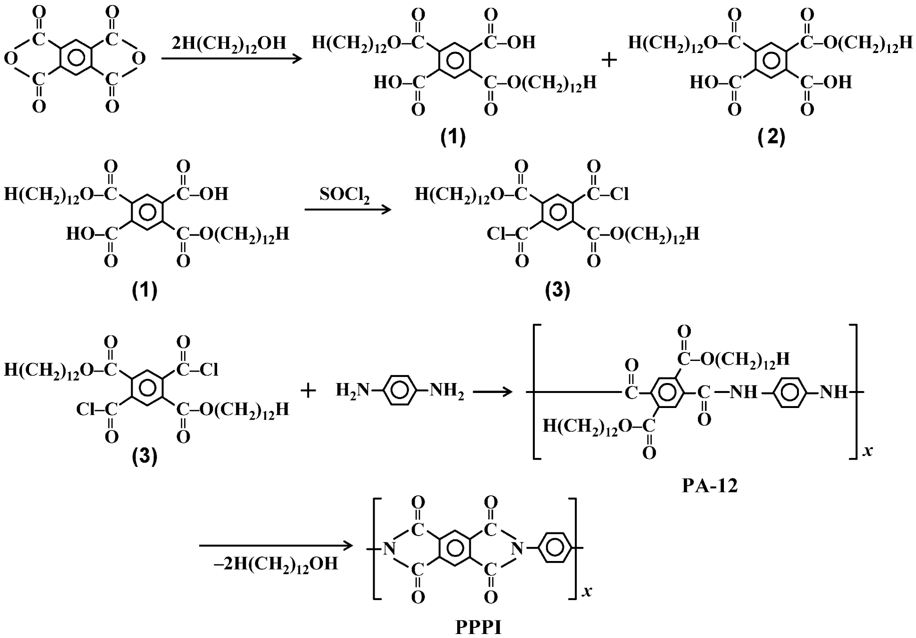
Following the above considerations, we have prepared rigid rodlike polyamide with flexible alkyl side chains. Para-linked aromatic poly(amic *n*-dodecyl ester) (PA-12), polymerized by polycondensation of 2,5-bis(1-dodecyloxy-carbonyl)terephthaloyl chloride and 1,4-diaminobenzene, have similar molecular structure with the rodlike polyesters by Watanabe et al. [8,9], and is expected to form the main-chain- and side-chain-segregated domains. As is well known, poly(amic alkyl ester)s have been used as precursor of polyimides because its chemical stability is better than that for poly(amic acid)s [15–22]. Thermal imidization of poly(amic alkyl ester)s with short alkyl chain length have been investigated in detail [15–21]. In this case, the cyclization reaction from the amic alkyl ester to imide ring occurs with removing alkyl alcohol. Kakimoto et al. [20] reported the structure and mechanical properties of poly(amic alkyl ester)s with long alkyl chains and poly(*p*-phenylene pyromellitimide) derived by thermal imidization, and succeeded to prepare oriented PI fiber with high tensile modulus by drawing the precursor fiber before imidization. On the other hand, there have been only limited reports about the chemical imidization of poly(amic alkyl ester)s [22].

The objective of this report is to perform the imidization reaction for PA-12 in solid-state. If the imidization reaction and removal of the alkyl chain proceed with maintaining the morphology of PA-12, the alkyl-chain-segregated domains in PA-12 will be transformed to cavities in fully aromatic polyimide, poly(1,4-phenylene pyromellite imide) (PPPI). For application use, these 'molecular cavity' may be suitable for separating membranes in order to separate substances by their molecular size. In this report, we have investigated the change of morphology formed by PA-12 after the chemical and thermal imidization reactions to PPPI by means of infrared spectrum, X-ray scattering, and density measurements.

2. Experimental

2.1. Materials

Outline of polymer synthesis is shown in Scheme 1 [4,18]. Twenty grams of pyromellitic dianhydride and equimolar 1-decanol was heated at 150 °C for 1 h. Because the reaction mixture contains *para* (**1**) and *meta* (**2**) isomers, 400 ml of acetone was added and stirred for 24 h in order to remove the *meta* isomer. This extraction process was repeated for three times. Finally, the precipitate was thoroughly washed with dichloromethane, and pure *para*



Scheme 1.

isomer, 2,5-bis(1-dodecyloxycarbonyl)terephthalic acid (**1**), was isolated. The purity was deterimed by ^{1}H NMR spectra (solvent: DMSO-d_6): the *para* isomer has two equivalent aromatic protons at 8.0 ppm, and *meta* isomer contains two inequivalent protons at 7.9 and 8.1 ppm.

The *para* isomer of di-*n*-dodecyl ester (**1**) (7.0 g) was added excess thionyl chloride (4 molar equiv.) and a drop of *N*,*N*-dimethylformamide, and heated to reflux for 2 h. After the reaction, the excess thionyl chloride was removed by distillation under reduced pressure. Residual thionyl chloride was further removed by adding benzene to the remaining solid and continuing the distillation. Finally, 2,5-bis(1-dodecyloxycarbonyl)terephthaloyl chloride, (**3**), was obtained as white solid after drying in vacuum.

1,4-diaminobenzene (0.54 g) was dissolved in hexamethylphosphoric triamide (HMPA) (10 ml) in three-necked round-bottomed flask. Benzene solution (10 ml) of propylene oxide (0.66 g) and dichloride of di-*n*-dodecyl ester (**3**) (2.997 g) was added to the flask at 0 °C, and stirred for 24 h at room temperature. After the polycondensation reaction, and viscous solution was diluted by HMPA/benzene mixture, and poured into excess methanol. The precipitated solid, PA-12, was washed in refluxing methanol for 30 min, filtered, and dried in vacuum.

As-cast film of PA-12 was prepared by casting the HMPA/benzene solution of PA-12 on flat glass plate, and the solvent was evaporated at 60–100 °C for 7 h under reduced pressure. Thickness of the obtained film was 1–2 μm.

Thermal imidization was conducted by heating the PA-12 film at elevated temperature under reduced pressure. Chemical imidization of the PA-12 film was conducted by soaking the film in pyridine or pyridine/toluene mixture at room temperature or 80 °C. After washing the film in toluene, the imidized film was dried in vacuum at 100 °C. Further heat treatment was performed at various temperatures under reduced pressure.

2.2. Measurements

Degree of imidization was investigated by Fourier transform infrared (FT-IR) spectra recorded with AVATAR 320-FT-IR (Nicolet). Wide-angle X-ray diffraction (WAXD) photographs were recorded with Ni-filtered Cu K_α radiation and a flat film as detector. The reflection spacing, d, was evaluated by using Bragg's equation, $2d\sin\theta=\lambda$, where 2θ and λ are scattering angle and wavelength of the X-ray beam (0.15418 nm), respectively. The value of 2θ was calibrated against the 111 reflection of silicone powder. Thermogravimetry analysis (TGA) was done using TG30 (Seiko Instruments) under nitrogen atmosphere with heating rate of 10 °C/min. Densities of the samples were determined by floatation method using potassium bromide aqueous solution.

3. Results and discussion

3.1. Layered structure of PA-12

WAXD measurement for as-cast PA-12 film was performed as the film surface is parallel to the incident X-ray beam, and the obtained WAXD photograph is shown in Fig. 1. A strong reflection with the spacing $d=1.6$ nm locates on equator line, and a weak reflection at $d=1.2$ nm is observed on meridional line. The spacing for the latter reflection coincides with the repeating distance of rodlike PA-12 along the molecular axis. This result suggests that PA-12 molecule is oriented parallel to the film surface, which seems reasonable because the rodlike polymers preferably lie on the film surface. Therefore, the strong reflection at $d=1.6$ nm should correspond to the intermolecular distance of PA-12. As reported by Watanabe et al. [9], the rodlike polyester with *n*-dodecyl side chains, PBpT-O12, exhibited hexagonal columnar mesophase and its *d*-spacing was observed at 2.34 nm. Extrapolation of the *d*-spacing for the layered mesophase of PBpT-O series with longer *n*-alkyl side chains estimates the *d* value as 1.8 nm for $n=12$. From these comparisons, PA-12 is most probably taking a layered structure in which the main-chain and side-chain-segregated layers are stacking repeatedly. It should be noted that there is amorphous halo around $d=0.44$ nm but no reflection from crystallized alkyl chain can be detected. Because the solvent evaporation was conducted at 100 °C, alkyl chain was in liquid state and was not crystallized even at room temperature.

3.2. Thermal imidization

Thermal properties and thermal imidization process for PA-12 was investigated by TGA measurement. As shown in Fig. 2, the decrease of sample weight starts around 160 °C, and the degree of the loss is about 55% in the range of 160–550 °C. This value shows good coincidence with the calculated weight loss of dodecanol during the thermal imidization and formation of PPPI. The second weight loss started at ~600 °C, corresponds to the degradation of PPPI.

According to the TGA results, thermal imidization reaction of PA-12 was performed at temperatures of 150 to

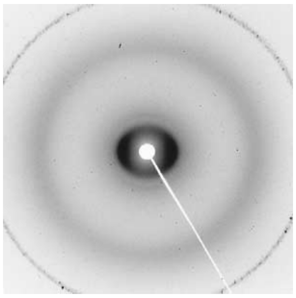


Fig. 1. WAXD photograph for as-cast film of PA-12. The normal of the film is placed in the horizontal direction.

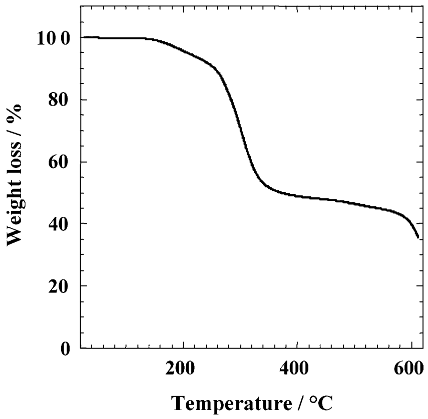


Fig. 2. TGA curve for PA-12 measured at the heating rate of 10 °C/min.

Table 1
Thermal imidization of PA-12

Temperature (°C)	α_{imide}	α_{alkyl}	ρ (g cm^{-3})
150	0.28	0.85	1.24
160	0.32	0.77	
170	0.42	0.68	
180	0.42	0.72	
190	0.39	0.71	
200	0.76	0.42	1.29
250	0.92	0.13	1.40
300	0.80	0.03	
350	0.85	0.02	1.46

375 °C under reduced pressure for 12 h. Progress of the imidization reaction was monitored by FT-IR spectrum. In Fig. 3(a), the IR spectrum of the as-cast PA-12 is indicated. We can recognize characteristic amide absorptions at approximately 3400 cm^{-1} for the N–H stretch, 1655 cm^{-1} for the amide carbonyl stretch (amide I), and absorption for C–H stretch in alkyl chain around 2800–3000 cm^{-1}. The sample after the thermal imidization at 350 °C is shown in Fig. 3(b). As the result of imidization and elimination of *n*-dodecanol, amide and alkyl absorptions disappeared and the characteristic imide absorptions begin to be observed at 1778 cm^{-1} for imide carbonyl stretch (imide I). Degree of progress of the imidization reaction from PA-12 to PPPI, α_{imide}, was evaluated by the peak height of imide I band at 1778 cm^{-1}, and the fraction of the remaining alkyl chain, α_{alkyl}, was evaluated by the absorption at 2922 cm^{-1}, with using the aromatic ring absorption at 1515 cm^{-1} as internal reference. As will be shown below, chemically imidized and subsequently heated sample showed highest degree of imidization and was defined as $\alpha_{\text{imide}}=1.0$. α_{imide} and α_{alkyl} are listed in Table 1, and plotted against the temperature for thermal imidization in Fig. 4. The value of α_{imide} and α_{alkyl} shows sharp increase and decrease, respectively, in the range of 190–200 °C. Fig. 5 shows the relation between α_{imide} and α_{alkyl} (●). The linear relationship along the straight line of $\alpha_{\text{alkyl}}=1-\alpha_{\text{imide}}$ suggests that the removal of 1-dodecanol occurs immediately after the formation of the imide ring.

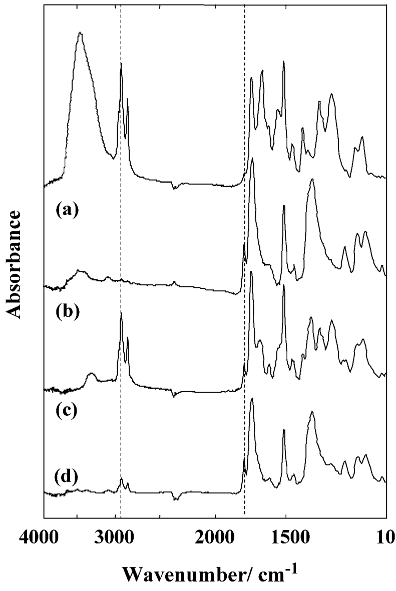


Fig. 3. FT-IR spectra for (a) PA-12, (b) thermally imidized sample at 350 °C, (c) chemically imidized sample in pyridine/toluene mixture at 80 °C for 96 h, and (d) the sample of (c) was heated at 200 °C.

WAXD patters for the thermally imidized samples are shown in Fig. 6. The strong reflection at $d=1.6$ nm, assigned to the repeating distance for layered structure, is still observed for the sample imidized at 150 °C as indicated by arrow in Fig. 6(a). However, this reflection becomes broad after imidized at 200 °C, and cannot be detected after the imidization above 250 °C as shown in Fig. 6(b). This means that the layered structure for PA-12 was not maintained by the thermal imidization reaction above 250 °C. Instead, sharp reflections at $d=0.60$ nm (indicated by the arrow in Fig. 6(b)) and 0.30 nm started to be appeared, these correspond to 002 and 004 reflections for the crystallized PPPI [23] . From these results, we can conclude that the layered structure in PA-12 cannot be maintained and densely packing of

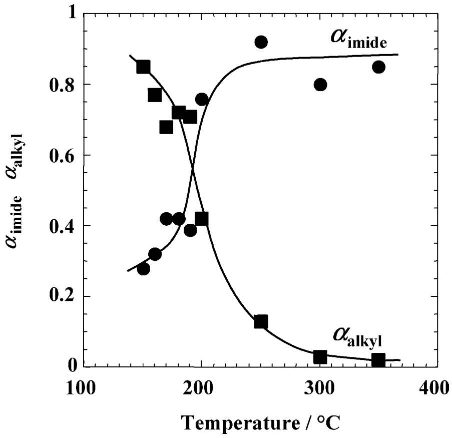


Fig. 4. Degree of imidization (α_{imide}, ●) and fraction of remained alkyl chain (α_{alkyl}, ■) plotted against temperature for thermal imidization.

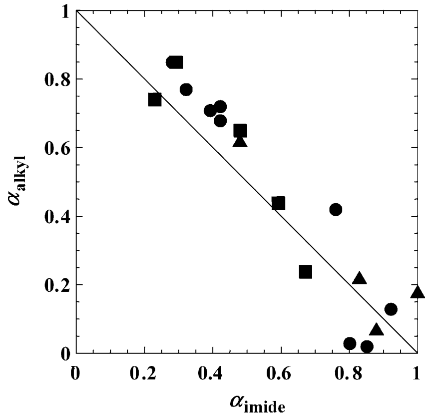


Fig. 5. α_{imide} vs. α_{alkyl} for thermally imidized (●), chemically imidized (■), and chemically imidized and subsequently heated samples (▲).

the PPPI chains occurs during the thermal imidization above 250 °C.

Results of density measurements for the thermally imidized samples are shown in Table 1. The density, ρ, for PPPI via poly(amic acid) has been reported in the range of 1.50–1.56 in Refs. [23–26]. As shown in Table 1, ρ values for PPPI prepared by high-temperature thermal imidization from PA-12 fall close to this range, but PPPI imidized at lower temperature exhibit smaller ρ value. In Fig. 7, ρ values are plotted against α_{imide} (●). Continuous line in the figure shows the calculated density with assuming the additive rule of PA-12 (1.15 g cm^{-3}) and PPPI via poly(amic acid) (1.53 g cm^{-3}). With the increase of α_{imide}, the density tends to increase to that for PPPI. However, some experimental values locate under the continuous line, means that the density cannot be represented by simple additive rule of PA-12 and PPPI and smaller than the expected. This result may suggest that, although the ordered layered structure cannot be detected from the WAXD pattern, the alkyl-chain-segregated domain still exists as a cavity after the imidization and removal of 1-dodecanol, which make the experimental density of PPPI lower than the predicted one from α_{imide}.

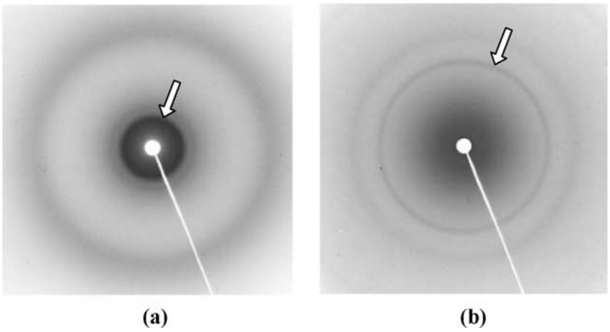

(a) (b)

Fig. 6. WAXD photographs for thermally imidized samples at (a) 150 °C and (b) 250 °C.

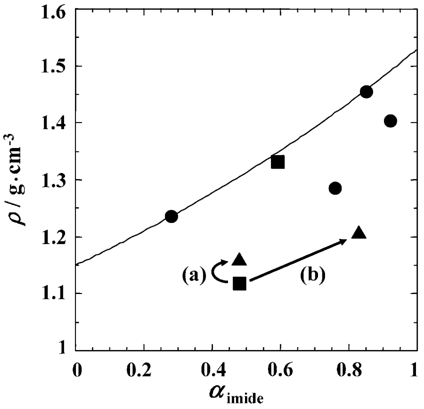


Fig. 7. Density for thermally imidized (●), chemically imidized (■), and chemically imidized and subsequently heated samples (▲, heated at 150 °C (a) and 200 °C (b)). The continuous line indicates the calculated density.

3.3. Chemical imidization

Solid-state chemical imidization was performed by soaking the PA-12 film in basic solvent, pyridine [22]. The imidization conditions are listed in Table 2, and the IR spectrum for the imidized sample no. 5 is shown in Fig. 3(c). As like that for the thermally imidized sample, decrease in amide absorption and increase in imide absorption can be recognized. α_{imide} and α_{alkyl} were also evaluated and listed in Table 2. Comparison of no. 1 and 3 suggest that the dilution of the base by toluene (volume ration of pyridine/toluene = 1:5) depress the imidization reaction. Decrease of the soaking time and temperature also decrease the value of α_{imide}. Plot of α_{imide} vs. α_{alkyl} for chemical imidization is shown in Fig. 5 by filled square. These plots also lie on the straight line, means that the elimination and removal of 1-dodecanol occurs as the progress of the imidization reaction. From these results, we can point out that the chemical imidization is a suitable method to control the degree of imidization.

WAXD patterns for these imidized samples of no. 2 and no. 5, shown in Fig. 8(a) and (b), respectively, indicate that the layered structure in PA-12 is respectively destroyed and maintained after the chemical imidization. From the comparison of the WAXD patters

Table 2
Chemical imidization of PA-12 at various conditions

No.	Solvent	Temperature	Time (h)	α_{imide}	α_{alkyl}	ρ (g cm^{-3})
1	Pyridine	80 °C	24	0.59	0.44	1.33
2	Pyridine	80 °C	96	0.67	0.24	
3	Pyridine/ toluene	80 °C	24	0.29	0.85	
4	Pyridine/ toluene	r. t.	96	0.23	0.74	
5	Pyridine/ toluene	80 °C	96	0.48	0.65	1.19

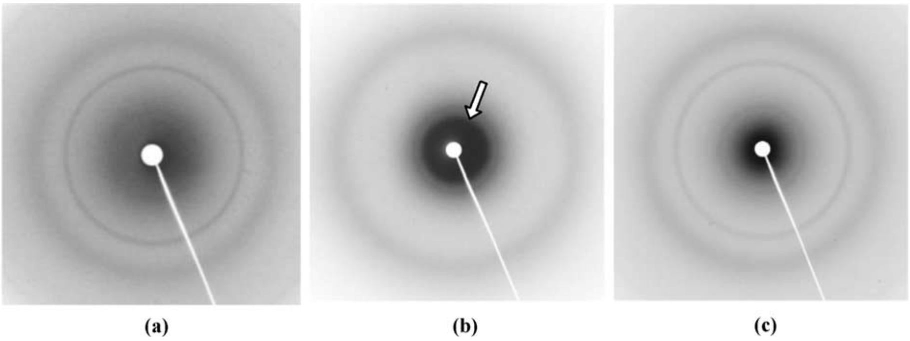


Fig. 8. WAXD photographs for chemically imidized samples of (a) no. 2, (b) no. 5, and (c) no. 5-2 in Tables 2 and 3. The arrow in (b) indicate the reflection at $d=1.6$ nm, assigned to the layered structure.

and the value of α_{imide}, maintenance of the layered structure seems to be achieved only when α_{imide} is less than 0.5.

The density after the chemical imidization is also listed in Table 2. Although the imidization for no. 5 proceeded to 48%, its density remained at almost same value for PA-12. We can point out that the imidized PA-12 of no. 5 contains a lot of cavity with maintaining the layered structure.

The sample of no. 5 in Table 2 was subsequently heated under vacuum for 12 h in order for progress of the imidization reaction. Temperatures for the thermal treatment are listed in Table 3, and the resulting α_{imide}, α_{alkyl}, and ρ values are also indicated. The thermal treatment at 150 °C did not influence these values as shown in no. 5-1 and arrow (a) in Fig. 7. On the other hand, heating above 200 °C accelerate the imidization reaction as shown in FT-IR spectrum in Fig. 3(d), which is consistent with the thermal imidization results in Table 1. It should be noted that the sample heated at 200 °C, no. 5-2 in Table 3 and arrow (b) in Fig. 7, exhibits small density value, 1.21 g cm^{-3}, instead of the high degree of imidization ($\alpha_{\text{imide}}=0.83$). This value is lower than that for thermally imidized sample at 200 °C.

The WAXD patter for this sample revealed that the reflection at $d=1.6$ nm, assigned to the layered structure, is disappeared (Fig. 8(c)). From these results, we may assume the solid-state structure of PPPI prepared from PA-12 as follows. Chemical imidization and elimination of 1-dodecanol by using pyridine as base progress in solid-state. If the alkyl chains are successfully removed with maintaining the layered structure, the density of PPPI should be smaller than that for PA-12. All the imidized samples in this report had larger ρ values than PA-12, so coagulation and packing of PPPI chains should be occurring to some extent. However, their densities are certainly smaller than that for the densely packed PPPI, suggesting the existence of cavity originated by the removal of alkyl chain. The degree of positional order of the layered structure become lower, and the cavity should be located randomly in PPPI. This low-density structure can be maintained until 200 °C because PPPI is rigid rodlike polymer with high glass transition temperature.

Table 3
Effect of the thermal treatment after the chemical imidization of PA-12[a]

No.	Temperature (°C)	α_{imide}	α_{alkyl}	ρ (g cm^{-3})
5-1	150	0.48	0.62	1.16
5-2	200	0.83	0.22	1.21
5-3	250	1.00	0.18	
5-4	300	0.88	0.07	

[a] All the samples was chemically imidized in pyridine/toluene at 80 °C for 96 h before the thermal treatment. Thermal treatment was performed at the indicated temperature for 12 h.

4. Conclusion

Structure change during solid-state thermal and chemical imidization of para-linked aromatic poly(amic *n*-dodecyl ester)s (PA-12) have been investigated. PA-12 formed the layered structure with main-chain-segregated and side-chain-segregated layers, and the repeating distance was 1.6 nm. Thermal imidization and base-catalyzed chemical imidization of PA-12 progressed with the formation of imide ring and elimination of 1-dodecanol in solid-state. The layered structure of PA-12 was destroyed during the imidization reaction when the degree of reaction was larger than 0.5. However, the obtained PPPI exhibited lower density than the predicted by simple additive rule of PA-12 and PPPI. This result may indicate that the side-chain-segregated domain was maintained as a cavity, as the result of the removal of side chains, surrounded by PPPI after the imidization reaction.

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