

First Synthesis of Both "Head-to-Head" and "Head-to-Tail" Polyimides Using a Common Unsymmetric Alicyclic Tetracarboxylic Dianhydride

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A structurally ordered polyimide with the main chain having the complete "head-to-tail" bonding sequence (**HTPI**) or the complete "head-to-head" bonding sequence (**HHPI**) was prepared. The synthesis was based on the unique reactivity of an unsymmetric spiroalicyclic tetracarboxylic dianhydride, *rel*-(1*R*,5*S*,6*R*)-spiro[3-oxabicyclo[3.2.1]octane-6,3′-tetrahydrofuran]-2,2′,4,5′-tetrone (**DAn**), which has one 5-membered and one 6-membered anhydride. Equimolar amount of amine reacts with this compound predominantly at the 6-membered ring. Thus, the reaction of **DAn** with 1 molar amount of 4-nitroaniline and the subsequent methanolysis and reduction gives a monomer for a head-to-tail polyimide, which was successfully converted to **HTPI** through a polycondensation-dehydration sequence. Additionally, a new dianhydride monomer **MHH**, which is a 2:1 adduct of **DAn** and *p*-phenylenediamine (**PPD**), was prepared. **MHH** was subjected to polycondensation with 1 molar amount of **PPD** and the condensate was dehydrated to give **HHPI**. Slow addition of **PPD** into the solution of **DAn** also afforded a semi head-to-head polyimide. The polyimides had inherent viscosity in the range of 0.20–0.73 dL/g and were characterized by NMR and IR spectra through a comparison with those of their random isomer **RPI**. No obvious differences in properties, such as solubility and thermal stability, between the ordered polyimides (**HTPI** and **HHPI**) and the random counterpart were found in this study.

Generally, polycondensation is carried out between two bifunctional monomers, XaaX and YccY, to give an -aacc- type product. In most cases, symmetric monomers are used and there is no isomerism concerning the orientation of the monomer unit in the main chain. However, when an unsymmetric monomer (XabX) rather than a symmetric one (XaaX) is employed for reaction with YccY, there might arise a different bonding sequence in the main chain, head-to-head (-baccab-, HH) and head-to-tail (-baccba-, HT).

Structurally ordered polymers (i.e., polymers having a complete HH or complete HT sequence in the main chain) are of interest from the viewpoint of the structure-property relationship. Pino et al. reported on the synthesis of a set of HH-, HT, and random polyamide having common repeating units, and compared the physical properties.[1] They also present theoretical aspects of the formation of ordered polycondensates by the reaction of a symmetric monomer with an unsymmetric one. Ueda et al.[2] explored the above theory through "fine tuning" of the monomers to other binary and ternary polycondensates including polyamides,[2a,2b] poly(amide-thioether)s,[2c] and poly(amine-thioether)s,[2g] as well as many copolyamides.[2d–2e]

In contrast, synthesis of ordered polyimides has been little investigated up to now. Some complete HT polyimides have been prepared using so-called AB-type monomers, namely, aminodi(carboxylic acid)s and their analogs.[3] Those monomers can generally be expressed as XacY, and their polycondensation gives -acac- type polyimides. Such polyimides intrinsically do not have HH- or random counterparts and are not suitable for the investigation of the structure–property relationship.

Kato et al. report the preparation of a series of strictly alternating HH copolyimides using a spiro[5.6]alicyclic dianhydride, **TCDA**, on the basis of the considerably different reactivity of the two anhydride groups.[4] Although **TCDA** could be applied in principle for the synthesis of HT- and random polyimides, this aspect of the work was not pursued further.

On the other hand, we have recently reported a synthesis of unsymmetric spirotricyclic dianhydride, *rel*-(1*R*,5*S*,6*R*)-spiro-[3-oxabicyclo[3.2.1]octane-6,3′-tetrahydrofuran]-2,2′,4,5′-tetrone (**DAn**), and its application to the polyimide synthesis.[5] During the model study for the polyimide, we found that the 6-membered anhydride ring in **DAn** is far more reactive than the 5-membered anhydride ring. This unique reactivity of **DAn** led us to investigate the synthesis of structurally isomeric ordered polyimides. This paper describes the first synthesis of a set of complete HT, complete HH, and random polyimides having common repeating units.

Experimental

Materials. **DAn** was synthesized according to the method reported in our previous paper.[5] *p*-Phenylenediamine (**PPD**), purchased from Tokyo Chemical Industry Co., Ltd., was purified by sublimation. *N*,*N*-Dimethylformamide (DMF) was purified by distillation under reduced pressure over calcium hydride and stored over 4A molecular sieves. Other reagents and organic solvents were of commercial grade and were used as received.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500 (^{1}H: 500 MHz; ^{13}C: 126 MHz) or JEOL JNM-LA400 (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectrometer. Chemical shifts are indicated in ppm units using tetramethylsilane as an internal standard, and the unit for the coupling constant *J* is Hz. IR spectra were measured using a JASCO IR-700 spectrometer on

KBr pellets. Elemental analyses were performed using a Fisons Instruments EA1108 CHN analyzer. Mass spectra were obtained on a JEOL JMS600 spectrometer. Melting points were determined by a differential scanning calorimetric analysis using a Rigaku DSC 8230 at a heating rate of 10 °C/min in a nitrogen atmosphere.

Inherent viscosity was determined using a Ubbelohde viscometer at a concentration of 0.5 g/dL in *N*-methyl-2-pyrrolidone (NMP) at 30 °C. Molecular weights of the polymers were estimated with a gel permeation chromatography (GPC) system equipped with a JASCO PU-1580 HPLC pump, a JASCO 875-UV detector and two Shodex GPC KF-806L columns, and were calibrated using standard polystyrene samples. Measurements were carried out at 40 °C using a 0.05 M LiCl/DMF solution as an eluent. A Rigaku differential scanning calorimeter DSC 8230 and a Rigaku differential thermogravimetric analyzer TG-8120 were used for thermal analyses. Differential scanning calorimetry (DSC) was conducted under a nitrogen stream at a flow rate of 100 mL/min and a heating rate of 20 °C/min. Thermogravimetric analyses (TGA) were carried out under a nitrogen flow of 100 mL/min with a heating rate of 10 °C/min. For the first runs in DSC and in TGA, the heating was stopped at 320 °C in nitrogen before the sample began to degrade. After being cooled to room temperature, the sample was subjected to the second run for the measurement of its thermal properties.

Monomer Synthesis. 1-Carboxymethyl-4-(4-nitrophenylcarbamoyl)-1,2-cyclopentanedicarboxylic Acid 1,1-Anhydride (1). In a 50-mL round bottomed flask were placed 4.032 g (18.0 mmol) of **DAn**, 2.484 g (18.0 mmol) of 4-nitroaniline and 20 mL of DMF. The resulting yellow solution was stirred magnetically at room temperature for 12 h. Removal of DMF under reduced pressure and drying under vacuum at room temperature afforded a yellow viscous oil. The oil was then subjected to silica gel column chromatography (eluent: EtOAc/Hexane/Acetone = 12/7/1). After the appropriate fraction was collected and the solvent was stripped off, the residue was dried under vacuum at 90 °C for 24 h to give 4.02 g (61% yield) of **1** as a pale yellow powder. TLC: R_f = 0.65 (EtOAc:AcOH = 96:4), mp 223 °C (DSC). IR (KBr) 3500–2500 (br), 3368, 3082, 1855, 1780, 1710, 1506, 1343, 854 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ 12.95 (br, 1H), 10.69 (s, 1H), 8.28 (d, 2H, J = 9 Hz), 7.91 (d, 2H, J = 9 Hz), 3.44 (dd, 1H, J = 12, 7 Hz), 3.35–3.28 (m, 1H), 3.18 (d, 1H, J = 19 Hz), 2.93 (d, 1H, J = 19 Hz), 2.54–2.44 (m, 3H), 2.16–2.09 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 177.1, 173.8, 172.3, 170.7, 145.3, 142.2, 125.0, 118.9, 53.9, 52.3, 42.1, 40.5, 38.5, 31.3. Anal. calcd for $C_{16}H_{14}N_2O_8$: C, 53.04; H, 3.89; N, 7.73%. Found: C, 52.52; H, 3.97; N, 7.60%. MS (FAB$^-$): 361 [(M−H)$^-$].

1-Carboxymethyl-1-methoxycarbonyl-4-(4-nitrophenylcarbamoyl)-2-cyclopentanecarboxylic Acid (2). In a 50-mL round-bottomed flask, 3.5 g (9.7 mmol) of **1** was dissolved in 40 mL of methanol to give a light yellow solution. It was then stirred and heated to reflux. After 2 h, a white powder began to precipitate out. The reflux was continued for another 1 h and then cooled to room temperature. The powder was collected by filtration and washed with cold methanol. The filtrate was condensed and kept refrigerated to afford more precipitate. The combined powders were dried under vacuum at 70 °C for 48 h to give compound **2** (2.6 g, 68%), mp 218 °C. IR (KBr) 3500–2500 (br), 3330, 3098, 2954, 1714, 1551, 1508, 1435, 1411, 1341, 1304, 855 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 12.38 (s, br, 1H), 10.56 (s, 1H), 8.20 (d, 2H, J = 9 Hz), 7.83 (d, 2H, J = 9 Hz), 3.62 (s, 3H), 3.12–3.01 (m, 2H), 2.73 (d, 1H, J = 17 Hz), 2.63 (d, 1H, J = 17 Hz), 2.49 (1H, overlapped by the solvent peak), 2.26–2.04 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.9, 173.23, 173.19, 172.1, 145.2, 142.0, 124.8, 118.8, 52.2, 52.1, 50.8, 48.6, 40.1, 37.7, 32.5. Anal. calcd for $C_{17}H_{18}N_2O_9$: C, 51.78; H, 4.60; N, 7.10%. Found: C, 51.60; H, 4.61; N, 7.11%. MS (FAB$^-$): 393 [(M−H)$^-$].

4-(4-Aminophenylcarbamoyl)-2-carboxymethyl-2-methoxy-carbonyl-1-cyclopentanecarboxylic Acid (MHT). In a 250 mL autoclave, the *p*-nitroanilide **2** (2.14 g, 5.43 mmol) was dissolved in 40 mL of THF and 20 mL of methanol. Platinum oxide (0.15 g, 0.66 mmol) was added to this solution and the mixture was stirred under 5×10^5 Pa of hydrogen at room temperature for 3 h. Insoluble materials were filtered off and the solvent was removed under reduced pressure at room temperature. Drying the residue in vacuo at room temperature for 48 h afforded **MHT** as a reddish solid, mp 156 °C. IR (KBr) 3500–2500 (br), 3424, 2956, 1725, 1663, 1551, 1515, 1420, 1318, 1209 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 9.60 (s, 1H), 7.21 (d, 2H, J = 9 Hz), 6.48 (d, 2H, J = 8 Hz), 3.62 (s, 3H), 3.07 (dd, 1H, J = 9, 8 Hz), 2.90 (m, 1H), 2.73 (d, 1H, J = 17 Hz), 2.66 (d, 1H, J = 17 Hz), 2.44 (dd, 1H, J = 14, 13 Hz), 2.16–2.09 (m, 1H), 2.02 (dd, 1H, J = 13, 13 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.9, 173.4, 172.1, 171.2, 144.5, 128.3, 120.8, 113.6, 52.3, 52.1, 51.0, 48.6, 43.0, 37.8, 32.7. MS (FAB$^+$): 365 [(M+H)$^+$].

Model Reaction of 2 with Aniline. In a 30-mL round-bottomed flask, 0.159 g (0.40 mmol) of **2** and 0.056 g (0.60 mmol) of aniline were dissolved in 2 mL of DMF. The solution was stirred at 75–85 °C under argon atmosphere for 3 h, and it was then cooled to room temperature. After DMF was removed under reduced pressure, a small portion of acetone was added to dissolve solids. Reprecipitation using water gave a white solid, which was collected by filtration and washed with water, then dried at 100 °C under vacuum for 20 h to afford compound **3** as a pale brown powder (0.050 g, 29%), mp 237 °C. IR (KBr) 3500–2500 (br), 3334, 3082, 2942, 1775, 1703, 1612 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 12.88 (s, br, 1H), 10.62 (s, 1H), 8.22 (d, 2H, J = 9 Hz), 7.86 (d, 2H, J = 9 Hz), 7.50 (dd, 2H, J = 8, 7 Hz), 7.42 (dd, 1H, J = 7 Hz), 7.22 (d, 2H, J = 8 Hz), 3.36–3.24 (m, 2H), 2.94 (d, 1H, J = 18 Hz), 2.63 (d, 1H, J = 18 Hz), 2.53–2.46 (1H, overlapped by the solvent peak), 2.43–2.36 (m, 1H), 2.29 (dd, 1H, J = 14, 4 Hz), 2.18–2.09 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.9, 174.6, 173.8, 172.2, 145.2, 142.0, 132.6, 128.8, 128.2, 126.8, 124.8, 118.8, 53.0, 51.2, 42.2, 40.2, 39.2, 31.2. Anal. calcd for $C_{22}H_{19}N_3O_7$: C, 60.41; H, 4.38; N, 9.61%. Found: C, 59.72; H, 4.34; N, 9.37%. MS (FAB$^-$): 436 [(M−H)$^-$].

8,8′-[1,4-phenylenebis(iminocarbonyl)]bis[1,3-dioxo-2-oxaspiro[4.4]nonane-6-carboxylic Acid] (MHH). A solution of 0.540 g (5.00 mmol) of **PPD** in 15 mL of acetone was added dropwise over 30 min at room temperature into a suspension of 2.240 g (10.00 mmol) of **DAn** in 20 mL of acetone. All of the solid went into the solution in 15 min. The mixture was stirred at room temperature for 24 h. Removal of acetone under reduced pressure afforded a pale yellow powder. The solid was reprecipitated by EtOAc/hexane and dried under vacuum at 130 °C for 24 h to give the monomer **MHH** (2.16 g, 77%) as a white powder, mp > 400 °C. IR (KBr) 3500–2500 (br), 3364, 3064, 2948, 1852, 1780, 1720, 1675, 1516 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6) δ 9.19 (s, 2H), 7.47 (s, 4H), 3.34 (dd, 2H, J = 13 Hz), 3.24–3.17 (m, 2H), 3.19 (d, 2H, J = 19 Hz), 2.90 (d, 2H, J = 19 Hz), 2.50–2.37 (m, 6H), 2.17–2.08 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 177.3, 173.2, 172.3, 170.7, 135.7, 120.5, 54.6, 53.6, 43.3, 41.9, 39.1, 32.6. Anal. calcd for $C_{26}H_{24}N_2O_{12}$: C, 56.12; H, 4.32; N, 5.04%. Found: C, 56.33; H, 4.63; N, 4.99%. MS (FAB$^-$): 555

[(M−H)$^-$]. HRMS (FAB$^-$): Found: 555.1284. Calcd. for $C_{26}H_{23}N_2O_{12}$ [(M−H)$^-$]: 555.1250.

Synthesis of Polymer. Synthesis of HTPI. In a 30-mL round-bottomed flask, 1.0 g (2.7 mmol) of **MHT** was dissolved in 6 mL of DMF to give a light yellow solution. The solution was heated to 130 °C and stirred at that temperature for 24 h under an argon atmosphere. The resulting viscous liquid was cooled to room temperature and treated as follows: one third was precipitated into methanol to give **HTPAA** as a white solid; IR (KBr) 3500–2500 (br), 1775, 1701, 1318 cm^{-1}. Another third was cast on a glass plate and dried at 50 °C under vacuum for 24 h, then it was heated at 100 °C for 1 h, at 200 °C for 1 h, and at 240 °C for 2 h under vacuum to afford a thermally imidized **HTPI** film. The remainder was subjected to chemical imidization: to the **HTPAA**/DMF solution, 4 mL of DMF, 3 mL of acetic anhydride and 2 mL of pyridine were successively added. The mixture was stirred at room temperature for 1 h, then heated at 130 °C and stirred for a further 5 h under argon. After cooling to room temperature, the resulting yellow solution was poured into 300 mL of methanol to precipitate the polymer as a white powder. The product was collected by filtration, washed with methanol, and then dried under vacuum at 130 °C overnight to give a chemically imidized **HTPI**, IR (KBr) 1779, 1710, 1362, 1328 cm^{-1}.

Synthesis of HHPI from MHH. In a 30-mL round-bottomed flask, 1.1130 g (2.00 mmol) of **MHH** and 0.2163 g (2.00 mmol) of **PPD** was dissolved in 6 mL of DMF to give a light yellow solution. The solution was stirred at room temperature under argon for 24 h, then it was heated to 90–100 °C and stirred for another 12 h. The resulting poly(amide acid) (**HHPAA**) solution was cooled to room temperature and treated using the methods as described for synthesis of **HTPI**, giving the solid **HHPAA**, IR (KBr) 3500–2500 (br), 1777, 1709 cm^{-1}, a thermally imidized **HHPI** film, and a chemically imidized **HHPI**, IR (KBr) 1779, 1713, 1362, 1328 cm^{-1}.

Synthesis of HH-rich Polyimide by Dropwise Addition of PPD to DAn Solution. In a 30-mL round-bottomed flask, 0.5600 g (2.50 mmol) of **DAn** was dissolved in 4 mL of DMF. To this solution, 0.2700 g (2.50 mmol) of **PPD** in 4 mL of DMF was added dropwise at room temperature in the following way: 2 mL of **PPD**/DMF solution was added during 15 min, then the mixture was stirred for 30 min, and the remainder of **PPD**/DMF solution was added dropwise during another 15 min. The mixture was stirred at room temperature under argon for 48 h to give a viscous solution. This solution was treated using the methods described for synthesis of **HTPI**, giving a solid **SAPAA**, IR (KBr) 3500–2500 (br), 1717, 1668, 1654 cm^{-1}, a thermally imidized **SAPI** film, and a chemically imidized **SAPI**, IR (KBr) 1779, 1715, 1688, 1361, 1328 cm^{-1}.

Results and Discussion

In our previous paper, we report that the reaction of **DAn** with 1 molar amount and 2 molar amount of aniline gave a single monoamide-monoanhydride-mono(carboxylic acid) and a single diamide-di(carboxylic acid), respectively.[5] The first aniline molecule attacked predominantly at 2-position of **DAn**, whereas the second equivalent of aniline attacked mainly on the carbonyl carbon at 5′-position. Although the reason is not clear, such a regioselective nature of the reaction makes it possible to synthesize both HH- and HT-polyimides along with a random one, according to Pino and Suter's theory.[1]

Synthesis of HT Polyimide. The synthesis of the HT polyimide was carried out as shown in Scheme 1. The route is based on the method often employed in the preparation of AB-type monomers for HT polyimides using a nitro group as a masked amino group.

The reaction of **DAn** with 1 molar amount of 4-nitroaniline gave a mixture of products. In the IR spectrum of the mixture, a peak at around 1820 cm^{-1} which could be attributed to C=O stretching of 6-membered anhydrides was not observed. The ^{1}H NMR of the mixture showed two amide proton peaks in a ratio of 7:3 at around 10 ppm. From these facts, the two compounds are identified as regioisomeric mono(amide acid)-monoanhydrides having a 5-membered anhydride ring. The major product was isolated by a silica gel column chromatography, and the structure was characterized to be **1** by its CH COLOC NMR analysis. It is worth mentioning that the 5-membered carboxylic anhydride was stable enough to endure the chromatographic conditions.

In order to avoid autocondensation during the monomer synthesis, the 5-membered anhydride should be transformed to another functional group, because anhydrides are hard to maintain in the presence of amines. Treatment of **1** in refluxing methanol gave a single half-ester having the structure shown in Scheme 1. It is noteworthy that the regioselectivity for the methanolysis of **1** was the opposite of that observed for the reaction of **DAn** with 2 molar amount of aniline; methanol attacked predominantly on the carbonyl carbon at 2′-position.

A one-pot methanolysis and hydrogenation could be possible in principle, because the reduction of the nitro group was carried out in THF/MeOH mixture. However, an attempted reaction using **1** resulted in the loss of regioselectivity for the methanolysis, which made both the purification and the analysis of the products significantly more difficult.

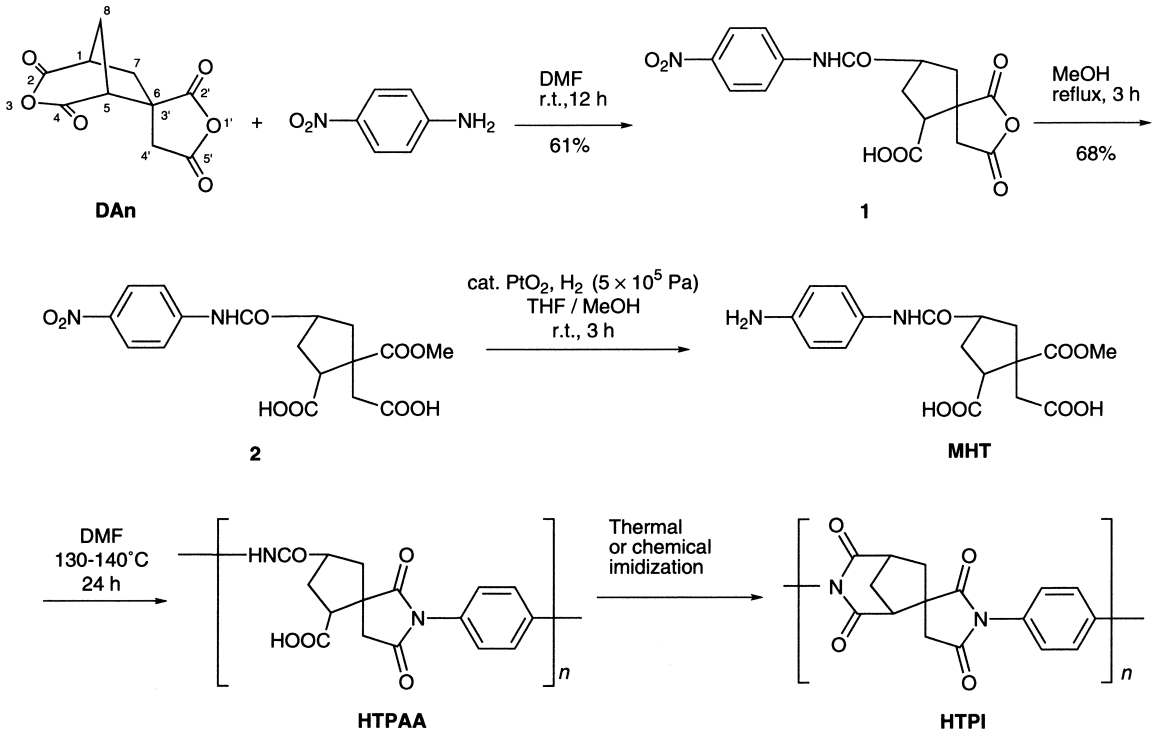
Thus, stepwise methanolysis and hydrogenation gave a new AB-type monomer **MHT** in a high yield. From this monomer, the residual solvent could not be removed even after drying under reduced pressure for one week at room temperature. Vacuum drying at 70 °C for 12 h gave rise to the condensation of **MHT** to some extent.

A model reaction was carried out using compound **2** and aniline at 80 °C in DMF. As the reaction proceeded, a precipitate was formed. The precipitate was found to be a mono(amide acid)-monoimide having a 5-membered imide ring. This indicates that concomitant ring closure is possible for the polycondensation of **MHT**.

Heating the **MHT**/DMF solution at 130 °C under argon for 24 h afforded a poly(amide acid) (**HTPAA**) first. The **HTPI** was obtained by either thermal or chemical imidization of the **HTPAA**. Formation of the polyimide was confirmed by IR and ^{1}H NMR analyses. Viscosity, molecular weights, and polydispersity indices of the chemically imidized **HTPI** are shown in Table 1. The polycondensation at the elevated temperature resulted in the increase in the molecular weight of the **HTPI** (Table 1, run 2).

Synthesis of HH Polyimide. Reaction of 2 molar amount of **DAn** with 1 molar amount of **PPD** resulted in the formation of a 2:1 adduct **MHH**. Although **MHH** should consist of two diastereomers, both its ^{1}H and ^{13}C NMR were quite simple and compatible with the structure shown in Scheme 2.

MHH was reacted with **PPD** to give a poly(amide acid)



Scheme 1.

Table 1. Inherent Viscosity and Molecular Weights of Ordered Polyimides Measured by GPC

Polyimide	η_{inh}/dL g^{-1}	$M_w/10^4$	$M_n/10^4$	M_w/M_n
HTPI[a)]	0.26	1.3	0.6	2.1
HTPI[b)]	0.32	3.1	1.7	1.8
HHPI	0.20	1.9	1.1	1.7
SAPI	0.73	10.9	5.3	2.1
RPI	0.79	8.0	4.5	1.8

a) Polycondensation was performed at 130 °C.
b) Polycondensation was performed at 170 °C.

(**HHPAA**). Usually, a polycondensation of dianhydride and diamine is performed at room temperature; however, it was found that heating was necessary for the reaction of **MHH** and **PPD**. As will be mentioned later, **HHPAA** contains a considerable amount of imide ring, perhaps due to the higher temperature necessary for polycondensation. The head-to-head polyimide **HHPI** was obtained by either thermal or chemical imidization of **HHPAA**.

According to Suter and Pino's theories,[1] a slow addition of the symmetric monomer to the unsymmetric one may also result in the production of nearly complete HH polycondensate provided that the reactivities of the two functional groups of the unsymmetric monomer are sufficiently different. Thus, we tried the slow addition method for the preparation of the semi head-to-head polyimide **SAPI**.

In order to compare with the ordered polyimides, a random polyimide (**RPI**) was synthesized by the method of adding the **DAn** powder in one portion to the **PPD**/DMF solution, according to the method described in our previous papers.[5,6]

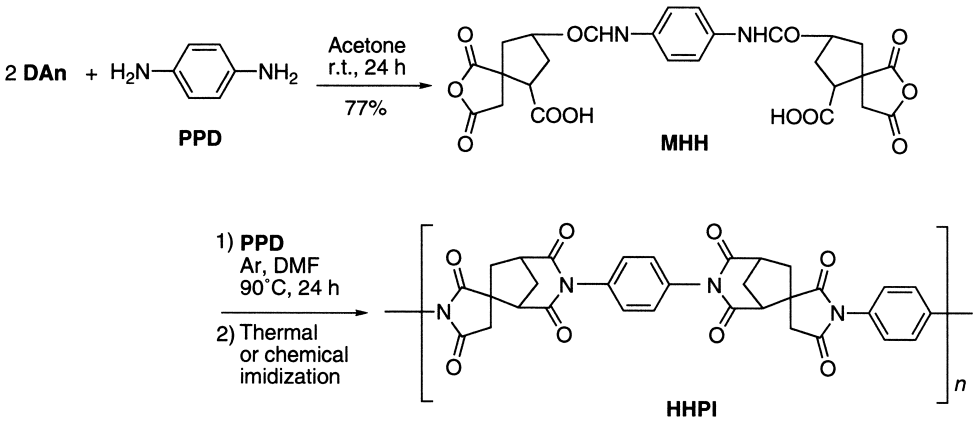
Characterization of Polyimides. Figure 1 shows the aromatic and amide proton regions in the ^{1}H NMR spectra of **HTPAA**, **HHPAA**, and **RPAA**.

For the spectrum of **HTPAA** (Figure 1a), two peaks in the Ar-H area can be attributed to the four protons of the aromatic ring. In the synthesis of this poly(amide acid), formation of the 5-membered imide ring in the main chain was anticipated from the model study. The presence of such an imide group in **HTPAA** was confirmed by its IR spectrum; a peak at 1775 cm^{-1}, which is due to C=O stretching of the 5-membered imide ring, appeared. Comparison of the integration values for the aromatic region and the amide N-H region in ^{1}H NMR indicated that the degree of imidization was 52%. This means that almost all of the 5-membered imide ring in the polymer chain was formed during the polycondensation step.

HHPAA showed four peaks in the Ar-H region of the ^{1}H-NMR spectrum (Fig. 1b). Similarly to **HTPAA**, the presence of the 5-membered imide ring was indicated by a 1777 cm^{-1} peak in the IR spectrum. By comparing integration values of the four peaks and that of the amide region, we suggested that the two outside smaller peaks in the aromatic region could be assigned to the phenylene group adjacent to the 5-membered imide ring, and that the content of the imide group was 64%. Just like **HTPAA**, the dehydrative ring closure to give the 5-membered imide might be completed at all positions in the main chain under the reaction conditions for the polycondensation of **MHH** and **PPD**.

The spectrum of **RPAA** was consistent with a superimposition of the spectra of **HTPAA** and **HHPAA** (Fig. 1c). The percentage of the imide ring was 55% for this random polyimide.

The appearance of the ^{1}H NMR spectrum of **SAPAA** was quite different from those of the above three poly(amide acid)s, and such a difference made it difficult to estimate the ori-



Scheme 2.

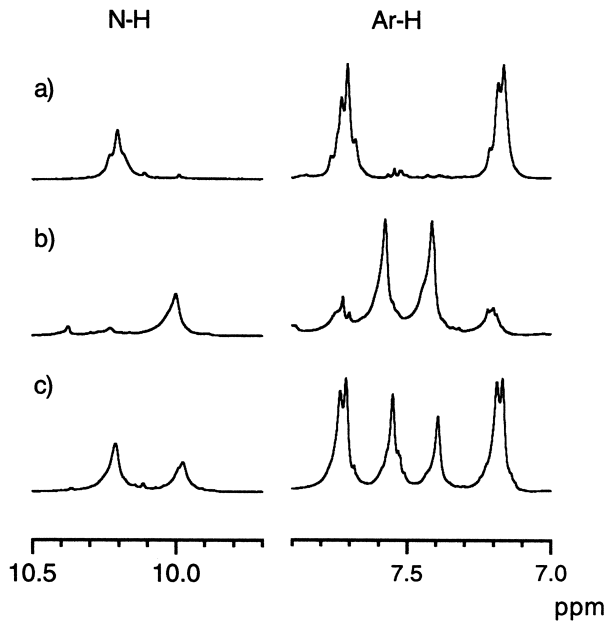


Fig. 1. Ar-H and N-H parts of the ^{1}H NMR spectra of (a) **HTPAA**, (b) **HHPAA**, and (c) **RPAA**.

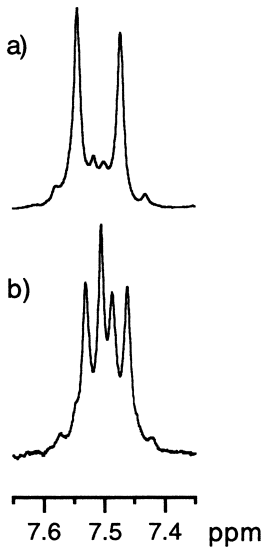


Fig. 2. Ar-H parts of the ^{1}H NMR spectra of (a) **SAPAA** and (b) **RPAA′**.

entational regularity of the monomer unit in **SAPAA** (Fig. 2a). This might be because of the absence of imide group in **SAPAA** due to the lower reaction temperature for polycondensation; the synthesis of **SAPAA** was performed at room temperature, whereas **HHPAA** and **RPAA** were synthesized at 90–100 °C and at 70 °C, respectively. In fact, the IR spectrum of **SAPAA** showed no peak assigned to the imide group. It is quite natural that the ^{1}H NMR of poly(amide acid) and that of poly[(amide acid)-imide] are different from each other.

In order to evaluate the regularity of the orientation of monomer unit in **SAPAA**, a standard ^{1}H NMR spectrum of random poly(amide acid) containing no imide ring is needed. The synthesis of such a poly(amide acid) was carried out at room temperature by mixing the two components simultaneously. As shown in Fig. 2b, the 1H NMR of polymer thus obtained (**RPAA′**) was quite different from that of **RPAA**. The aromatic region of the ^{1}H NMR of **RPAA′** showed four peaks, with two outside peaks identical to those observed in the spectrum of **SAPAA**. The others might be attributed to the aromatic protons of the HT sequence moieties. On the basis of this assignment, the regularity of **SAPAA** is concluded to be quite high.

Figure 3 shows the Ar-H areas of the ^{1}H NMR spectra of the chemically imidized **HTPI**, **HHPI**, **SAPI**, and **RPI**. A nice consistency was again observed for the spectrum of **RPI** and the superimposition of those of **HTPAA** and **HHPAA**. As expected, the spectrum of **SAPI** was quite similar to that of **HHPI**, despite the difference between the ^{1}H NMR spectra of **HHPAA** and that of **SAPAA**.

The appearance of the aromatic region in the ^{1}H NMR of **SAPI** was considerably affected by both the concentration of the solution and the molecular weight of **SAPI**. Figures 3c and 4a are the spectra of **SAPI** having different molecular weights; the inherent viscosity for **SAPI** used in Fig. 3c and Fig. 4a was 0.46 and 0.73 dL/g, respectively.

In Fig. 4, the spectra of the DMSO-d_6 solution of the same **SAPI** in several concentrations are depicted. At lower concentration, the pattern of the NMR became closer to that of **HHPI**, which has the η_{inh} value of 0.20 dL/g. These facts suggest that an inter- and an intramolecular aggregation of **SAPI** bring

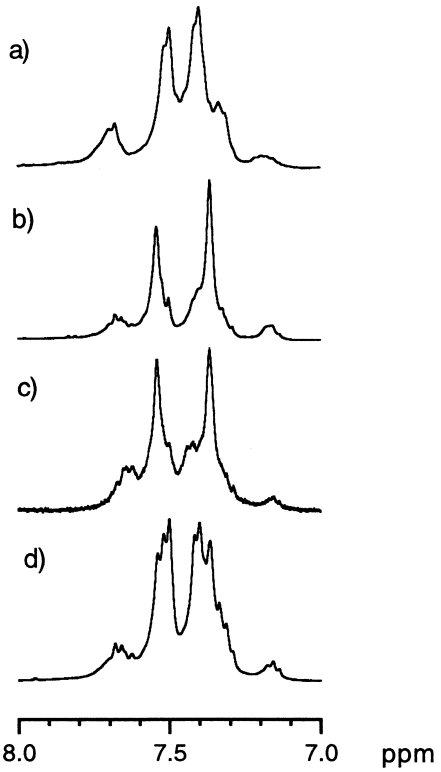


Fig. 3. Ar-H parts of the ^{1}H NMR spectra of (a) **HTPI**, (b) **HHPI**, (c) **SAPI**, and (d) **RPI**.

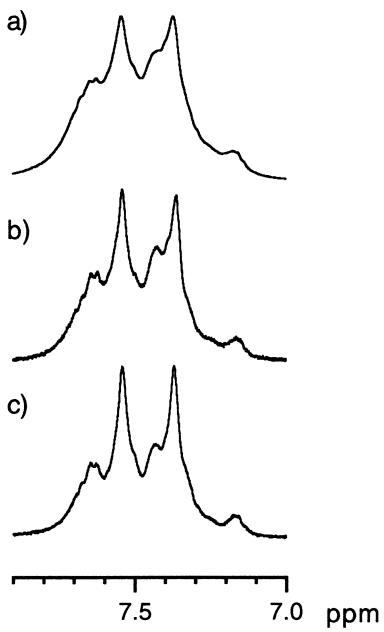


Fig. 4. Ar-H parts of the ^{1}H NMR spectra of **SAPI** (η_{inh} = 0.73 dL/g). The concentrations of the samples were (a) 7 $\times 10^{-2}$ g/mL, (b) 5 $\times 10^{-3}$ g/mL, and (c) 4 $\times 10^{-4}$ g/mL.

about the change in the NMR pattern. Such an aggregation was also suggested in the GPC measurement; when DMF containing no lithium chloride was used as an eluent, the apparent molecular weight of the polyimide was $> 10^6$.

Properties of Polyimides. All the chemically imidized polyimides synthesized in this study exhibited good solubility in aprotic solvents, such as DMSO, NMP, DMF, and DMAc; no significant differences in the solubility were found between the ordered polyimides (**HTPI**, **HHPI** and **SAPI**) and the random one (**RPI**). No glass transitions were observed for any of the polyimides before they began to degrade, which was consistent with the results in our previous papers.[5,6] The thermal degradation temperatures (T_d) are summarized in Table 2. Polyimides synthesized in this study had T_d values in a rather narrow range of 420–431 °C.

Table 2. Properties of the Ordered Polyimides

Polyimide	T_d[b)]/°C	Film property
HTPI	424	brittle
HHPI	428	brittle
SAPI	425	flexible
RPI[a)]	430	flexible

a) Results from Ref. 6.
b) For chemically imidized polyimides.

Transparent colorless films were obtained for all the thermally imidized polyimides except **HTPI**, which was pale yellow probably because of the high temperature in the polycondensation step. Films of **HTPI** and **HHPI** were somewhat brittle compared to the films of **SAPI** and **RPI**, probably because of the lower molecular weights of **HTPI** and **HHPI**.

In conclusion, we first synthesized the ordered polyimide isomers which have the complete "head-to-tail" bonding sequence (**HTPI**) and the complete "head-to-head" bonding sequence (**HHPI**). Differences in the solubility and thermal properties between the ordered polyimides and their random counterpart were not found for the present system using **PPD** as the diamine unit, probably because of the rigidity of the main chains that prevents the close packing for all polyimides regardless of the regularity of the orientation of the monomer unit in the main chain. The effect resulting from the loose packing of the main chains is much stronger than the effect resulting from the regularity of the orientation. It can be expected that use of a flexible diamine unit may result in obvious differences in properties between the ordered polyimides and the their random isomer. On the other hand, the ordered polyimides are regular in monomer orientation in the polymer chain, but random in the stereochemistry. **DAn** is a chiral compound, and so the regularity in the stereochemistry would be of importance to realize obvious difference in the physical properties between isomeric polyimides. Further studies including the homochiral version of this study and a one-pot synthesis of altered copolyimides are now under way in this laboratory.

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References

1 a) P. Pino, G. P. Lorenzi, U. W. Suter, P. G. Casartelli, A. Steinmann, F. J. Bonner, and J. A. Quiroga, *Macromolecules*, **11**,

624 (1978). b) U. W. Suter and P. Pino, *Macromolecules*, **17**, 2248 (1984). c) G. Xie, P. Pino and G. P. Lorenzi, *Macromolecules*, **23**, 2583 (1990). d) F. T. Gentile, W. R. Meyer, and U. W. Suter, *Macromolecules*, **24**, 633 (1991). e) W. R. Meyer, F. T. Gentile, and U. W. Suter, *Macromolecules*, **24**, 642 (1991).

2 a) M. Ueda, M. Morishima, M. Kakuta, and J. Sugiyama, *Macromolecules*, **25**, 6580 (1992). b) M. Ueda and H. Sugiyama, *Macromolecules*, **27**, 240 (1994). c) M. Ueda and T. Okada, *Macromolecules*, **27**, 3449 (1994). d) M. Ueda, A. Takabayashi, and H. Seino, *Macromolecules*, **30**, 363 (1997). e) O. Haba, H. Seino, K. Iguchi, K. Aoki, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 2309 (1998). f) L. Li, H. Seino, K. Yonetake, and M. Ueda, *Macromolecules*, **32**, 3851 (1999). g) L. Li, T. Hayakawa, K. Yonetake, and M. Ueda, *Macromol. Chem. Phys.*, **201**, 1667 (2000).

3 a) Z. Y. Wang, Y. Qi, T. P. Bender, and J. P. Gao, *Macromolecules*, **30**, 764 (1997). b) G. I. Nosova, T. I. Zhukova, M. M. Koton, L. A. Laius, and Y. N. Sazanov, *Vysokomol Soedin*, **A26**, 998 (1984). c) W. A. Feld, L. Serico, B. G. Genez, and L. L. Friar, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 833 (1983). d) J.-K. Im and J.-C. Jung, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 3530 (1999). e) J.-K. Im and J.-C. Jung, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 402 (2000).

4 J. Kato, A. Seo, and S. Shiraishi, *Macromolecules*, **32**, 6400 (1999).

5 J. Li, J. Kato, K. Kudo, and S. Shiraishi, *Macromol. Chem. Phys.*, **201**, 2289 (2000).

6 J. Li, K. Kudo, and S. Shiraishi, *Macromol. Rapid Commun.*, **21**, 1166 (2000).