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NOTES

Synthesis of Sequential Polyamide by Direct Polycondensation II.

Mitsuru UEDA, Makoto MORISHIMA, and Mayumi KAKUTA

Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992, Japan

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As part of our research program on the synthesis of condensation polymers by a direct polycondensation,[1] our group have recently initiated the synthesis of sequential polyamide by the direct polycondensation.

In the preceding paper,[2] we reported a method for the synthesis of sequential polyamide (head-to-head, or tail-to-tail). This polymer was prepared by the direct polycondensation of symmetric monomer (YccY), isophthalic acid with nonsymmetric monomer (XabX), 2,6-dimethyl-*p*-phenylenediamine using the activating agent, diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphate (**1**).

In our continuing investigation of versatility of this method, we now report a successful synthesis of sequential (head-to-head or tail-to-tail) polyamide by the direct polycondensation of isophthalic acid (**2b**) with 2-(4-aminophenyl)ethylamine (**5**) using the activating agent **1**.

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidone (NMP) was purified by vacuum distillation and stored over 4-A molecular sieves. Benzoic acid (**2a**) and isophthalic acid (**2b**) were purified by recrystallization. 2-(4-aminophenyl)ethylamine (**5**) was purified by vacuum distilation (116°C/1 mmHg). Triethylamine (TEA) was purified by a usual method. Other reagents and solvents were obtained commertially and used as received.

The activating agent diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphate (**1**) was prepared according to the reported procedure.[3]

N,N'-Di(2-phenylethyl)isophthalamide (**4**). The activating agent **1** (0.422 g, 1.1 mmol) was added to a solution of **2b** (0.0831 g, 0.5 mmol) and TEA (0.14 ml) in NMP (1.0 ml) at room temperature. After 10 min, 2-phenylethylamine (**3**) (0.121 g, 1 mmol) was added. Stirring of the mixture was continued for 1 h, and poured into 10% aqueous sodium hydrogen carbonate. The precipitate was filtered, washed with water, and dried. The yield was 0.182 g (98%). Recrystallization from aqueous methanol afforded white leaflets. mp 172—172°C. IR (KBr): ν 3290 (N–H), 1640 cm^{-1} (C=O). ^{13}C NMR [$(CD_3)_2SO$]: 165.5 ppm (C=O). *Anal.* Calcd for $C_{24}H_{24}N_2O_2$: C, 77.39%; H, 7.52%; N, 6.50%. Found: C, 77.24%; H, 7.49%; N, 6.58%.

2-[4-(N'-Benzoylamino)phenyl]-N-benzoylethylamine (**6**). This compound was prepared from **5** (0.068 g, 0.5 mmol) and **2a** (0.122 g, 1 mmol) as described above. The yield was 0.159 g (93%). Recrystallization from methanol yielded white crystals. mp 226°C (by DTA) (lit.[4] 223°C). IR (KBr): ν 3230 (N–H), 1640 cm^{-1} (C=O). ^{13}C NMR [$(CD_3)_2SO$]:

165.9, 165.1 ppm (C=O).

N-Phenyl-N'-(2-phenylethyl)isophthalamide (**9**). The activating agent **1** (0.422 g, 1.1 mmol) was added to a solution of 3-carboxybenzanilide **8** (0.243 g, 1 mmol), **3** (0.121 g, 1 mmol), and TEA (0.14 ml, 1 mmol) in NMP (1.0 ml) at room temperature. The solution was stirred for 1 h at this temperature. The product was isolated as described above. The yield was 0.170 g (99%). Recrystallization from aqueous methanol yielded white leaflets. mp 185—186°C. IR (KBr): ν 3320 (N–H), 1650 cm^{-1} (C=O). ^{13}C NMR [$(CD_3)_2SO$]: 165.4, 164.8 ppm (C=O). *Anal.* Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72%; H, 5.85%; N, 8.13%. Found: C, 76.77%; H, 6.01%; N, 7.96%.

POLYMER SYNTHESIS

Authentic Polyamide (**11**)

N,N'-Di[2-(4-aminophenyl)ethyl]isophthalamide (**10**). A solution of **1** (0.805 g, 2.1 mmol), **2b** (0.166 g, 1 mmol), and TEA (0.28 ml, 2 mmol) in NMP (1.0 ml) was added dropwise at room temperature with stirring to a solution of **5** (0.272 g, 2 mmol) in NMP (0.5 ml). The addition was completed in 30 min, and stirring of the mixture was continued for an additional 1 h. The solution was poured into 10% aqueous sodium hydrogen carbonate (100 ml). A precipitate formed, and it was collected by filtration, washed with water, and dried *in vacuo*. The yield was 0.362 g (90%). Recrystallization from benzonitrile produced white crystals. mp 154—157°C. IR (KBr): ν 3300 (N–H), 1640 cm^{-1} (C=O). *Anal.* Calcd for $C_{24}H_{20}N_4O_2$: C, 71.62%; H, 6.51%; N, 13.92%. Found: C, 71.63%; H, 6.43%; N, 13.70%.

The activating agent **1** (0.422 g, 1.1 mmol) was added to a solution of **10** (0.202 g, 0.5 mmol), **2b** (0.0831 g, 0.5 mmol), LiCl (0.0013 g, 0.03 mmol), and TEA (0.14 ml, 1 mmol) in NMP (1 ml). The mixture was stirred for 24 h at room temperature. The resulting viscous solution was diluted with NMP (2—3 ml) and poured into methanol (200 ml). The polymer that precipitated was filtered and was refluxed in methanol for 2 h. The polymer was collected and dried *in vacuo* at 80°C. The yield was 0.266 g (100%). The inherent viscosity of the polymer in NMP was 0.32 dl g^{-1} at a concentration of 0.5 g dl^{-1} at 30°C. IR (KBr): ν 3240 (N–H), 1640 cm^{-1} (C=O). *Anal.* Calcd for $(C_{16}H_{14}N_2O_2 \cdot 1/2\ H_2O)_n$: C, 69.74%; H, 5.49%; N, 10.18%. Found: C, 70.59%; H, 5.32%; N, 9.81%.

Random Polyamide (**12**) *from Isophthaloyl Chloride and* **5**. A solution of **5** (0.136 g, 1 mmol) and TEA (0.28 ml, 2 mmol) in NMP (0.5 ml) was cooled to a mush with a dry ice-acetone bath. To this was added a solution of isophthaloyl chloride (0.203 g, 1 mmol) in NMP (1 ml) in one portion, and the cooling bath was changed to an ice-water bath. The mixture was stirred for 24 h. The polymer was isolated as described above. A 96% yield of the polymer having an inherent viscosity of 0.34 dl g^{-1} in NMP (C=0.5 g dl^{-1} at 30°C) was obtained. IR (KBr): ν 3250 (N–H), 1650 cm^{-1} (C=O). *Anal.* Calcd for $(C_{16}H_{14}N_2O_2 \cdot 1/2\ H_2O)_n$: C, 69.74%; H, 5.49%; N, 10.18%. Found: C, 69.53%; H, 5.37%; N. 9.89%.

Polyamide **13** *from* **2b** *and* **5**. To a solution of **5** (0.136 g, 1 mmol) in NMP (0.5 ml) was added dropwise at room temperature a solution of **2b** (0.166 g, 1 mmol), TEA (0.28 ml, 2 mmol), and **1** (0.805 g, 2.1 mmol) in NMP (1 ml). The addition was 30 min, and stirring of the mixture was continued for 24 h. The polymer was isolated as described above. The yield was 0.270 g (100%). The inherent viscosity was 0.30 dl g^{-1} in NMP (C=0.5 g dl^{-1} at 30°C). IR (KBr): ν 3240 (N–H), 1650 cm^{-1} (C=O). *Anal.* Calcd for $(C_{16}H_{14}N_2O_2 \cdot 1/2\ H_2O)_n$: C, 69.74%; H, 5.49%; N, 10.18%. Found: C, 69.99%; H, 5.39%; N, 9.67%.

RESULTS AND DISCUSSION

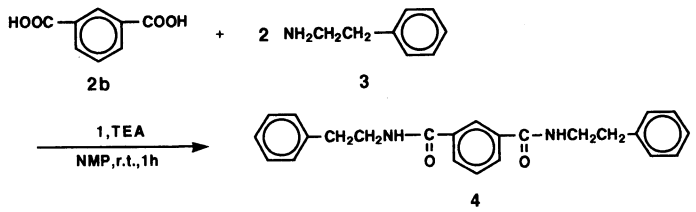
Model Reaction

The synthesis of sequential polyamide

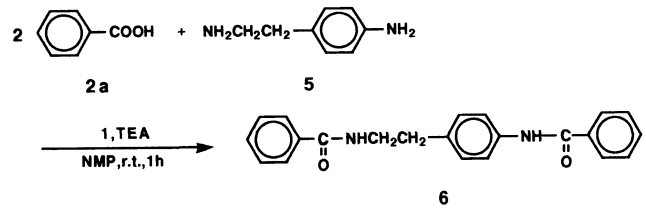
(head-to-head or tail-to-tail) from XabX and YccY monomers requires that the ratio of rate constants for the reactions of functional groups of nonsymmetric monomer XabX, $r=k_{bx}/k_{ax}$ should be small. In the previous paper,[5] we measured the overall second order rate constant (k) for the reaction of **2a** with various anilines in NMP in the presence of **1**, and found that there is a linear relationship with a slope of 1 between $\log k$ and pK_a of aniline derivatives. As the difference of pK_a values between an aliphatic amine and an aromatic amine is about 5, the rate constants for the aminolysis of the active intermediate will be changed by more than 10^5 when the amine is varied from the aliphatic amine to the aromatic amine. Thus, 2-(4-aminophenyl)ethylamine (**5**) was chosen as the XabX monomer for the polycondensation.

Prior to the synthesis of sequential polyamides, the following model compound work was performed by the direct procedure to determine if the model compounds were formed in quantitative yields to constitute a polymer-forming reaction. This procedure consists of the addition of **1** to a solution of a carboxylic acid and an amine in NMP that contains a tertiary organic base to form a carboxylate anion.

The reaction of isophthalic acid **2b** with 2-phenylethylamine **3** and that of benzoic acid **2a** with 2-(4-aminophenyl)ethylamine **5** were studied (eq 1 and 2).



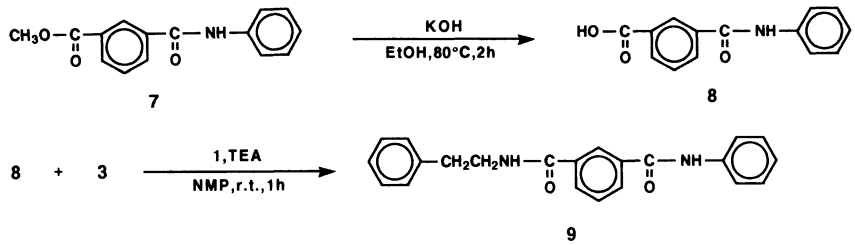
(1)



(2)

The reactions afforded the model compounds, *N*,*N*′-di(2-phenylethyl)isophthalamide (**4**) and 2-[4-(*N*′-benzoylamino)phenyl]-*N*-benzoylethylamine (**6**) in quantitative yields.

To clarify the structure of sequential polyamides, the following model compound *N*-phenyl-*N*′-(2-phenylethyl)isophthalamide (**9**) was also prepared from **3** and 3-carboxybenzanilide (**8**) which was obtained by alkaline hydrolysis of 3-methoxycarbonylbenzanilide (**7**) (eq 3).

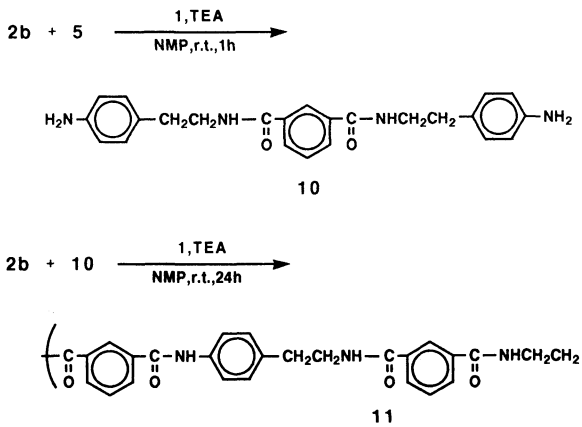


(3)

Polymer Synthesis

Synthesis of Authentic Polyamides. The authentic polyamides, such as head-to-head or tail-to-tail and random polyamides were synthesized for characterization of the structure of sequential polyamides obtained by the direct polycondensation.

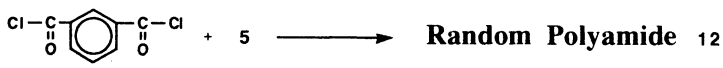
The authentic polyamide (**11**), as head-to-head or tail-to-tail polyamide was prepared by the direct polycondensation of **2b** with *N*,*N*′-di[2-(4-aminophenyl)ethyl]isophthalamide (**10**) which was obtained from **2b** and **5** (eq 4).



(4)

The polycondensation proceeded smoothly and gave the polyamide **11** with inherent viscosity of 0.32 dl g^{-1}.

The random polyamide **12** was synthesized from isophthaloyl chloride and **5** by the low temperature solution polymerization. Polycondensation was carried out in NMP by mixing both monomers all at once (eq 5).



(5)

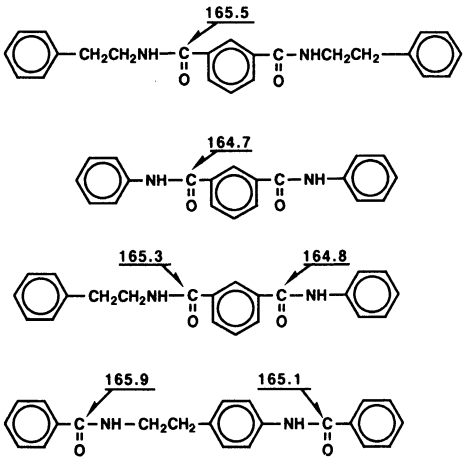
Synthesis of Sequential Polyamide (head-to-head, or tail-to-tail) **13**. As described in the preceding paper,[2] if XabX monomer is mixed all at once with YccY monomer, where we have arbitrary chosen -aX to be the faster reacting group ($r \ll 1$), only random polymer can be obtained. To obtain the head-to-head or tail-to-tail polymer, YccY should be added slowly to XabX, that is, if YccY is added slowly to XabX so that there will never be any unreacted -cY groups. After half of the YccY is added, the only XbaccabX will be produced. Upon addition of the rest of YccY, only -bccb- structures will be formed. Accordingly, the resulting polymer will contain -acca- and -bccb- arrangements only, and the probability of two adjacent nonsysmmetric units in a chain to point in the same directions, *s*, is zero.[2]

The direct polycondensation of **2b** with **5** in the presence of **1** was carried out at room temperature by the slow addition of **2b** to **5**, and gave polyamide **13** with inherent viscosity of 0.30 dl g^{-1}.

Polymer Characterization

The polymer **13** was defined as the expected sequential polyamide by comparing its IR spectrum with those of model compounds. The IR spectrum exhibited characteristic absorption at 3300 due to the NH streching and two strong absorptions at 1640 and 1540 cm^{-1}, which are assigned to amide I and amide II bands. Elemetal analyses also supported the formation of the expected polymer.

The microstructure of polymer was determined by means of ^{13}C NMR spectroscopy. ^{13}C NMR chemical shifts of amide carbonyl groups for model compounds are shown in Scheme 1.



Scheme 1.

The ^{13}C spectra of polyamide **13** and random polyamide **12** are presented in Figures 1 and 2, respectively. The spectrum of polyamide **13** was identical to that of polyamide **11**. The resonances with CO chemical shifts in the amides between 164.5 and 165.5 ppm, are assigned, as shown in the inset in Figure 1, on the basis of assignments for the model compounds.

On the other hand, the four peaks of carbon nuclei in amide carbonyl groups for polyamide **12** were observed at 165.5, 165.4, 164.6, and 164.5 ppm (Figure 2) as would be expected from its random structure.

These results clearly indicate that the direct polycondensation of **2b** with **5** produced the desired head-to-head or tail-to-tail ($s \simeq 0$) polyamide.

The polyamides were white solids, soluble in sulfuric acid, methanesulfonic acid, and dipolar aprotic solvents, such as NMP, DMF, and

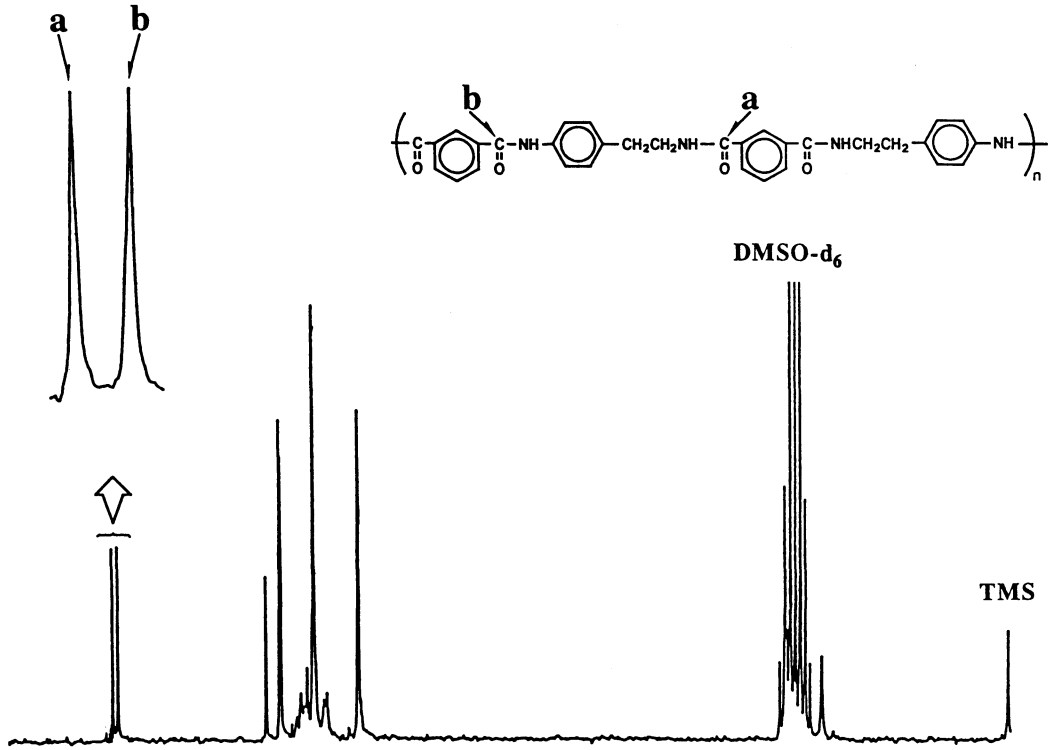


Figure 1. ^{13}C NMR spectra of polyamide **13** in $[(CD_3)_3SO]$ at 25°C.

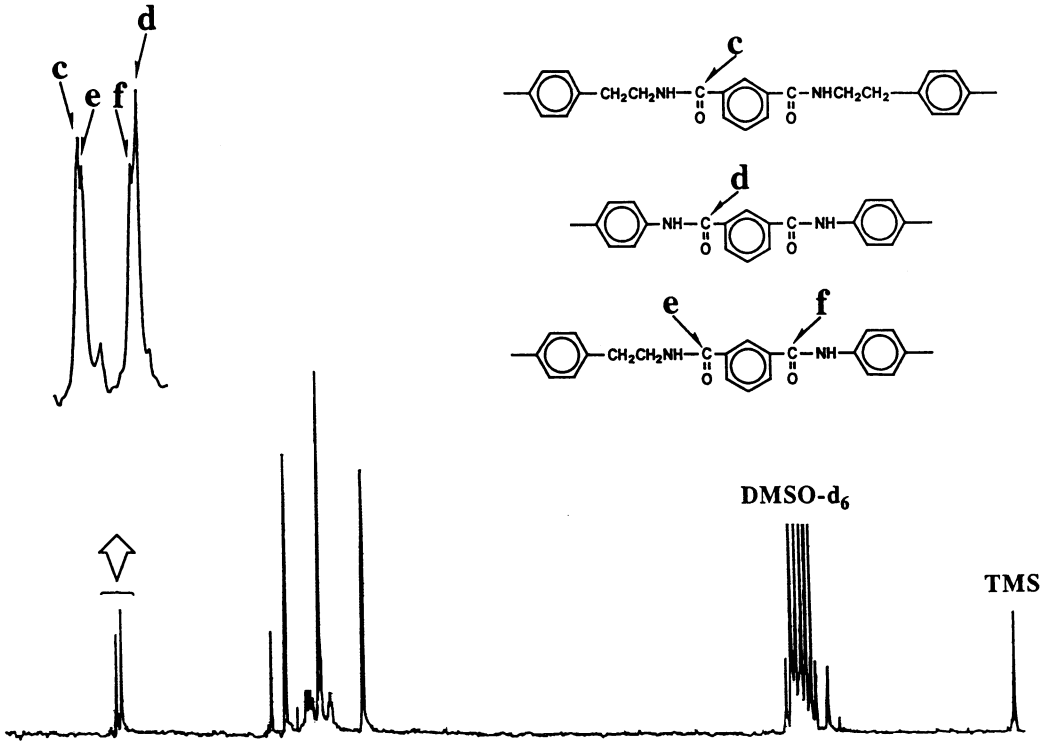


Figure 2. ^{13}C NMR spectra of polyamide **12** in $[(CD_3)_3SO]$ at 25°C.

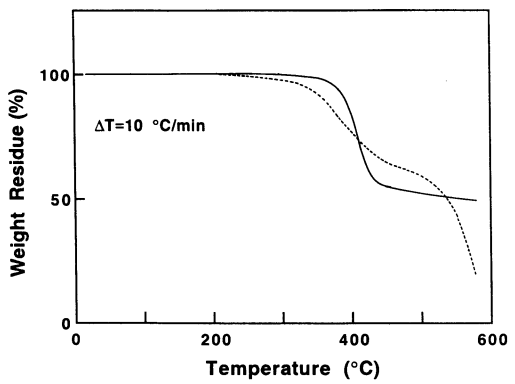


Figure 3. TG curves of polyamide **13** in nitrogen (——) and in air (– – – –).

DMSO.

The thermal stability of the polymer was examined by thermogravimetry (TG). A typical trace for the polymer is shown in Figure 3. The polymer **13** showed a 10% weight loss in air and nitrogen at 360°C and 390°C, respectively. We expected the difference in their properties owing to different regularity. However, no difference in the solubility and thermal stability among these polyamides can be detected. Pino *et al.*[6] observed a similar behavior for the studies of the influence of constitutional isomerism on the physical propereties of polycondensate, and reported that unsubstituted polyamides might not be very suitable because strong effects brought about by extensive interchain NH···OC bonds might mask subtle effects due to isomerism.

In summary, our studies indicate that the polyamide having a head-to-head or tail-to-tail sequence can be readily prepared by the direct polycondensation of symmetric monomer **2b** with nonsymmetric monomer **5** by using the activating agent **1**.

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