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Optically Active Polyamides Having an (−)-Anti Head-to-Head Coumarin Dimer Component. 1. Synthesis, Characterization, and Optical Properties

Kazuhiko Saigo,* Yun Chen, Noriyuki Yonezawa, Toshio Kanoe, Kouzou Tachibana, and Masaki Hasegawa*

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan. *Received July 12, 1985*

ABSTRACT: A series of optically active polyamides (**3a–f**) was prepared from the (−)-anti head-to-head coumarin dimer **1** by a ring-opening polyaddition reaction with hexamethylenediamine (**2a**), *N,N′*-dimethylhexamethylenediamine (**2b**), 1,3-xylylenediamine (**2c**), piperazine (**2d**), 4,4′-oxybis[aniline] (**2e**), and 1,4-phenylenediamine (**2f**). Model diamides corresponding to these polyamides were also synthesized as reference compounds. A TG–DSC study showed that these polyamides were almost amorphous with a decomposition temperature at ca. 250 °C in a nitrogen stream. On the basis of the optical rotation and circular dichroism (CD) spectra of these polyamides, **3e** and **3f** were found to exist in ordered conformation in *N,N′*-dimethylacetamide (DMAc) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and in aqueous NaOH solutions. This results from the electronic repulsion between the phenolate anions formed by the bases. Moreover, the abnormal dextrorotatory optical rotation of **3d** in DMAc solution is interpreted as correlated to its very rigid structure.

Introduction

A number of optically active natural polymers, such as polypeptides, polynucleotides, and polysaccharides, are well-known to play important functions in life by their highly ordered conformation, which is caused by various interactions between functional groups. So far, many attempts have been made to synthesize optically active artificial polymers that could exist in highly ordered conformation in solution similar to natural polymers.[1] Optical activity based on macromolecular asymmetry has been recently reported for polyaldehydes,[2-4] poly(triphenylmethyl methacrylate),[5-7] and polyisocyanates or polyisonitriles with a 1,3-dioxolane pendant group.[8] Helical dissymmetric polymers differ from biological macromolecules in that the monomer can be achiral. Overberger and his co-workers synthesized a series of optically active rigid polyamides having optically active diacid and/or diamine components in the main chain and found that on addition of a small amount of strong acid the ordered conformation of specific polyamides can be changed drastically by protonation of the amide carbonyl.[9]

In the previous paper, we reported the synthesis of racemic polyamides from anti head-to-head coumarin dimer.[10] We also reported the successful resolution of the racemic coumarin dimer into a pair of optically active forms,[11] which can be useful components for a new type of optically active polyamides. Since such polyamides inevitably contain crowded and rigid cyclobutane rings in the main chain in addition to the interacting functional groups of phenyl, phenolic hydroxyl, and amide linkage, it is expected that these polyamides would form ordered conformations in solution depending on the structure of the diamine component. Moreover, their ordered conformations would change reversibly with change in the basicity of the medium. Previously, from this viewpoint, the conformation of the polyamides derived from (−)-anti head-to-head coumarin dimer **1** in solution was briefly studied on the basis of their optical rotation properties.[12]

In this paper, we wish to report in detail on the preparation of optically active polyamides from **1** and several diamines and on the thermal and conformational properties of these polyamides.

Experimental Section

Measurements. The melting points of model diamides were determined on a Laboratory Devices Mel-Temp and are uncorrected. The inherent viscosity was measured at 30 °C with an Ostwald viscometer. The concentration was 0.30 g/dL in DMAc. ^{1}H NMR spectra of model diamides and polyamides were measured in Me_2SO-d_6 by using a Hitachi R-40 spectrometer. Infrared spectra of model diamides were measured with a Jasco IR-810 infrared spectrophotometer. Gel permeation chromatography (GPC) of the polyamides was performed at 50 °C on a Shodex PAK AD-80M/S column, using a 0.01 M LiBr solution of DMAc as an eluent with the flow rate of 0.5 mL/min. A molecular weight calibration curve was obtained by using standard polystyrene: $\bar{M}_n = 289 \times 10^4$ ($\bar{M}_w/\bar{M}_n = 1.09$), $\bar{M}_n = 42.2 \times 10^4$ ($\bar{M}_w/\bar{M}_n = 1.05$), $\bar{M}_n = 10.7 \times 10.7 \times 10^4$ ($\bar{M}_w/\bar{M}_n = 1.01$), $\bar{M}_n = 4.39 \times 10^4$ ($\bar{M}_w/\bar{M}_n = 1.01$), $\bar{M}_n = 1.67 \times 10^4$ ($\bar{M}_w/\bar{M}_n = 1.02$), $\bar{M}_n = 6200$ ($\bar{M}_w/\bar{M}_n = 1.04$), and $\bar{M}_n = 2800$ ($\bar{M}_w/\bar{M}_n = 1.05$). TG–DSC curves were recorded on a Rigaku Denki Thermoflex TG-DSC instrument under a nitrogen stream with the heating rate of 5 °C/min for 6–8 mg of sample. The optical rotations of polyamides and diamides were measured with a Jasco DIP-360 digital polarimeter at about 15 °C in a 1-dm cell at a sample concentration of ca. 0.15 g/dL in DMAc and 0.37 M aqueous NaOH. The circular dichroism (CD) and UV spectra were measured in an 0.10-cm cell at room temperature on a Jasco J-500 spectropolarimeter and on a Shimadzu UV-260 spectrophotometer, respectively. Measurements were carried out just after the sample was dissolved completely. The concentration was 5.0×10^{-4} (repeating unit mol)/L in both DMAc and 0.2 M aqueous NaOH except for **3d** and **3e** (2.0×10^{-4} (repeating unit mol)/L). All CD data are given in cm^2/(repeating unit mmol).

Materials. (−)-Anti head-to-head coumarin dimer **1** was obtained from the racemate by the diastereomeric resolution method as reported in a previous paper.[11] Before use, **1** was recrystallized from benzene and dried at 60 °C in vacuo (ca. 2 mmHg) for 24 h: $[\alpha]^{21}_{D}$ −9.0° (*c* 1.00, benzene), almost 100% enantiomeric excess on the basis of HPLC analysis of its diamide derivative with (*S*)-(−)-1-phenylethylamine.[11]

N-Methylhexylamine (**2b**) was synthesized by the diborane reduction reported by Brown and Heim.[13] Other diamines and amines are of commercial origin. The diamines **2a–c** and all of the amines were predried with NaOH pellets and then purified by distillation under reduced pressure just before the polymerization or the diamide synthesis. The diamines **2d–f** were purified by recrystallization from benzene followed by drying at 50 °C in vacuo (ca. 2 mmHg) for 24 h.

DMAc was predried with 4-Å molecular sieves and then distilled under reduced pressure before use (85–88 °C (34 mmHg)).

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (pure reagent: Nakarai Chemicals, Ltd.) was used without further purification.

Ring-Opening Polyaddition Reaction. In this study, hexamethylenediamine (**2a**), *N,N′*-dimethylhexamethylenediamine (**2b**), 1,3-xylylenediamine (**2c**), piperazine (**2d**), 4,4′-oxybis[aniline] (**2e**), and 1,4-phenylenediamine (**2f**) were used as diamine components. The diamine (ca. 3 mmol) was placed in a 30-mL two-necked flask that was evacuated and then filled with argon

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Table I
Ring-Opening Polyaddition Reaction of 1 with Diamines[a,b]

						^{1}H NMR δ[f]			
	time, h	yield, %	η_{inh},[c] dL·g^{-1}	$10^{-4}\bar{M}_n$[d]	IR ν,[e] cm^{-1}	cyclobutane ring[g]	ArOH[h]	aromatic	other
3a	21	76 (89)	0.88 (0.99)	5.0	1638 1540 752	3.2–3.8 4.3–4.8	9.32	6.3–7.3 (m, 8 H)[i]	0.5–1.2 (br, 8 H) 2.3–3.1 (br, 4 H)
3b	14	84 (80)	0.35 (0.27)	1.8	1615 755	3.8–4.3 4.3–4.9	9.35	6.3–7.3 (br, 8 H)	0.6–1.4 (br, 8 H) 2.3–2.9 (br, 6 H) 2.9–3.6 (br, 4 H)
3c	21	86 (100)	0.63 (0.73)	2.1	1645 1530 755	3.5–3.9 4.5–4.9	9.29	6.2–7.2 (m, 12 H)	3.7–4.3 (br, 4 H) 7.4–7.9 (br, 2 H)
3d	24	97 (96)	0.51 (0.70)	2.2	1598 750	3.8–4.2 4.4–4.8	9.42 9.71	6.4–7.3 (br, 8 H)	3.30 (s, 8 H)
3e	24	65	0.31	2.6	1650 1525 751	3.6–4.0 4.6–4.9	9.2–9.6[j]	6.3–7.4 (br, 16 H)	9.2–9.6[j]
3f	24	86 (92)	0.36 (0.37)	2.0	1650 1550 753	3.5–4.0 4.5–5.0	9.1–9.4[j]	6.3–7.3 (m, 12 H)	9.1–9.4[j]

[a] Concentration of 0.50 mol/L in DMAc, reaction temperature of 80 °C. [b] Yield and inherent viscosity in parentheses are those of corresponding racemic polyamides. [c] 0.30 g/dL in DMAc at 30 °C. [d] By GPC calibrated with standard polystyrene. [e] By KBr pellet method. [f] Measured at a concentration of ca. 30-mg sample in 0.4 mL Me$_2$SO-d_6. [g] 4 H, two broad peaks. [h] 2 H, singlet. [i] Two amide protons were overlapped. [j] Amide protons and phenylhydroxyl protons were overlapped.

three times, and DMAc was added with a syringe to prepare a clear solution of ca. 0.5 mol/L concentration. With gentle stirring, a stoichiometric quantity of finely powdered 1 was added to the solution at once. The mixture was heated to 80 °C in an oil bath with stirring under an argon atmosphere. After ca. 24 h of heating, the reaction mixture was diluted with 10 mL of DMAc and coooled to room temperature. The solution was added dropwise to 200 mL of methanol, and the precipitate that appeared was collected by filtration. The precipitate was treated with methanol in a Soxhlet extractor for 3 h to remove residual DMAc. In the case of **3f**, the precipitate was dissolved in 200 mL of 0.2 M NaOH solution and then acidified with 1.0 M aqueous HCl solution in an ice bath. The resulting precipitate was collected by filtration and then washed successively with 1.0 M aqueous HCl solution, water, and acetone. The polyamides thus obtained were finely pulverized and dried in vacuo at 60–80 °C over phosphorous pentoxide overnight. The polyamides were all identified by ^{1}H NMR and IR spectra. The results are summarized in Table I.

Anal. Calcd for **3a**: $(C_{24}H_{28}O_4N_2)_n$: C, 70.57; H, 6.91; N, 6.86. Found: C, 67.10; H, 6.73; N, 6.88. Anal. Calcd for **3b**: $(C_{26}H_{32}O_4N_2)_n$: C, 71.54; H, 7.39; N, 6.42. Found: C, 69.80; H, 6.89; N, 6.33. Anal. Calcd for **3c**: $(C_{26}H_{24}O_4N_2)_n$: C, 72.88; H, 5.65; N, 6.54. Found: C, 71.83; H, 5.70; N, 6.52. Anal. Calcd for **3d**: $(C_{22}H_{22}O_4N_2)_n$: C, 69.83; H, 5.86; N, 7.40. Found: C, 66.13; H, 6.14; N, 7.51. Anal. Calcd for **3e**: $(C_{30}H_{24}O_5N_2)_n$: C, 73.16; H, 4.91; N, 5.69. Found: C, 68.63; H, 4.71; N, 5.42. Anal. Calcd for **3f**: $(C_{24}H_{22}O_4N_2)_n$: C, 71.99; H, 5.54; N, 7.00. Found: C, 69.24; H, 5.02; N, 6.77.

The discrepancy in carbon analysis, which is also observed for other polyamides containing a cyclobutane ring, seems to be the inherent character of **3a–f** and would be attributed to the carbonization of the aromatic groups.

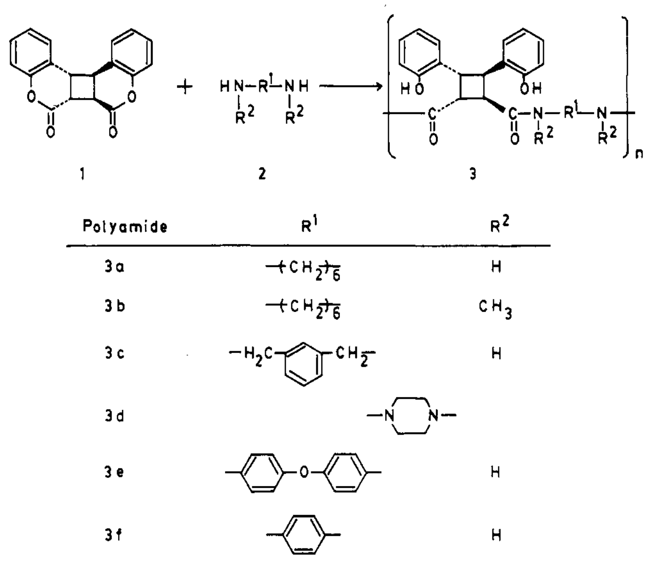
Synthesis of Model Diamide Compounds (5). The corresponding model diamides were synthesized by the method reported in our previous paper,[14] using hexylamine (**4a**), *N*-methylhexylamine (**4b**), 3-methylbenzylamine (**4c**), piperidine (**4d**), 4-methoxyaniline (**4e**), and aniline (**4f**) as amines.

A typical reaction of 1 with the amine is described as follows: A solution of 1 (585 mg, 2 mmol) and the aliphatic amine (16 mmol) in dioxane (6 mL) was heated at 60 °C for 2 h. After the solution cooled to room temperature, a white precipitate was collected by filtration, recrystallized from acetone, and dried in vacuo (ca. 2 mmHg) for 24 h. When **4e** or **4f** was used, the reaction time was prolonged to 4 h. The diamides were all identified by ^{1}H NMR and IR spectra. The results are listed in Table II.

Results and Discussion

Preparation of Optically Active Polyamides. As expected from the high reactivity of the lactone groups in (−)-dimer 1, optically active linear polyamides with high

Scheme I



Scheme II

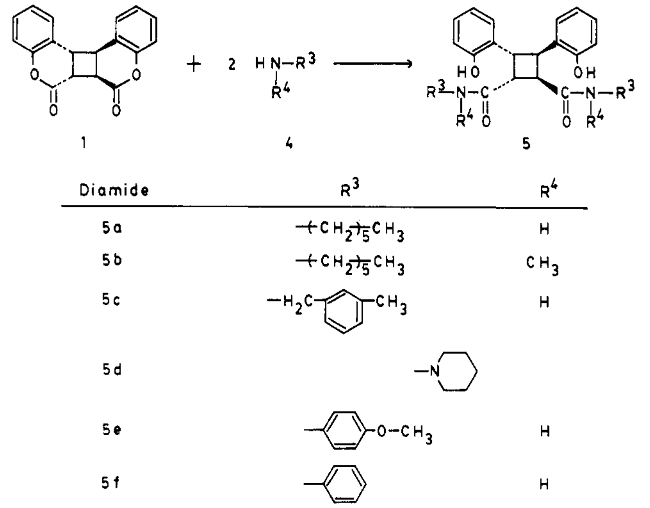


Table II
Lactone-Opening Reaction of 1 with Amines

	yield, %	mp, °C	IR ν,[a] cm^{-1}	^{1}H NMR δ[b]: cyclobutane ring[c]	ArOH[d]	aromatic	other
5a	98	173–174	1625 1530 750	3.55, 4.65	9.36	6.5–7.2 (m, 10 H)[e]	0.5–1.2 (m, 22 H) 2.4–3.0 (m, 4 H)
5b	84	203–205	1595 755	4.05, 4.62	9.33	6.4–7.2 (m, 8 H)	0.6–1.4 (m, 22 H) 2.63 (s, 6 H) 3.0–3.4 (m, 4 H)
5c	54	200–235[f]	1635 1528 754	3.70, 4.83	9.40	6.5–7.2 (m, 16 H)	2.21 (s, 6 H) 3.89 (dd, J = 15, 6 Hz, 2 H) 4.20 (dd, J = 15, 6 Hz, 2 H) 7.81 (dd, J = 5.5, 6 Hz, 2 H)
5d	86	249–250	1583 750	4.06, 4.65	9.43	6.6–7.3 (m, 8 H)	0.4–1.5 (m, 12 H) 2.7–3.5 (m, 8 H)
5e	96	213–215	1646 1510 754	3.86, 4.80	9.48	6.5–7.4 (m, 16 H)	3.68 (s, 6 H) 9.34 (s, 2 H)
5f	46	210–212	1642 1532 756	3.90, 4.81	9.48	6.5–7.4 (m, 18 H)	

[a] By KBr pellet method. [b] Measured at a concentration of ca. 30-mg sample in 0.4 mL Me$_2$SO-d_6. [c] 4 H, two pseudodoublets. [d] 2 H, singlet. [e] Two amide protons were overlapped. [f] Decomposition.

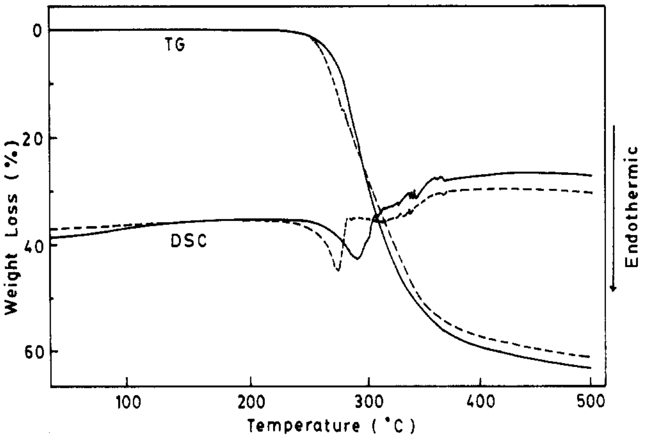


Figure 1. TG–DSC curves of **3f** (—) and its racemic counterpart (- - -).

Table III
Mean Residue Rotations ([*m*]) of Polyamides and Molar Rotations ([*M*]) of Model Diamides Derived from 1[a]

polyamide [diamide]	η_{inh}, dL·g^{-1}	$[m]_D$ ($[M]_D$) DMAc	$[m]_D$ ($[M]_D$) aq NaOH	$[m]_{435}$ ($[M]_{435}$) DMAc	$[m]_{435}$ ($[M]_{435}$) aq NaOH
3a	0.88	–241	–465	–657	–1253
[**5a**]		(–295)	(–687)	(–757)	(–1643)
3b	0.35	–437	–581	–1096	–1508
[**5b**]		(–474)	*b*	(–1159)	*b*
3c	0.63	–115	–310	–340	–857
[**5c**]		(–180)	(–480)	(–411)	(–1249)
3d	0.51	+116	*c*	+172	*c*
[**3d′**][d]	0.15	–14	–261	–109	–737
[**5d**]		(–391)	(–649)	(–989)	(–1722)
3e	0.31	–451	–181	–1314	–681
[**5e**]		(–523)	(–880)	(–1476)	(–2406)
3f	0.36	–358	+1115	–1041	+2941
[**5f**]		(–456)	(–898)	(–1336)	(–2417)

[a] Rotation angles were measured at ca. 0.15 g/dL in DMAc and 0.37 M aqueous NaOH solution. [b] The optical rotations were not measured due to its insolubility in aqueous NaOH. [c] The values could not be measured since the polyamide was immediately hydrolyzed to give low molecular weight material. [d] Low molecular weight **3d** recovered from aqueous NaOH solution.

molecular weight were easily obtained by the ring-opening polyaddition reaction of **1** and diamines. The polymerization of **1** with **2a** and **2c** proceeded at a higher rate than that with **2b**, **2d**, **2e**, and **2f**, and the reaction mixtures became viscous within 1 h; the resulting polyamides also exhibited higher inherent viscosities than the other polyamides (Table I). This reflects the sensitivity of the polymerization to the nucleophilicity of the diamine. All the polyamides were cast from a solution on a glass plate, giving transparent and flexible films, which is indicative of their linear structures with high molecular weights.

All the polyamides have poor solubility in nonpolar and protic polar solvents, and even good solvents for polyamide like 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol cannot dissolve these polyamides completely. But aprotic polar solvents such as DMAc, Me$_2$SO, and NMP can dissolve these polyamides easily. Moreover, they readily dissolve in aqueous alkaline solutions, showing them to be optically active polyelectrolytes. These optically active polyamides have a higher solubility in DMAc than their racemic counterparts except for **3f**.

The TG-DSC curve of a representative polyamide, **3f**, is shown in Figure 1. The optically active polyamides showed primarily similar thermal behavior to the corresponding racemic polyamides[10] and decompose at about 250 °C in a nitrogen stream. These polyamides are glassy amorphous polymers despite their optical activity. Large endothermic peaks at the decomposition temperature of the polyamides **3e** and **3f** seem due to the high stability of amide linkages, which can delocalize their unpaired electrons through the benzene rings.

Optical Rotational Behaviors in Solution. As summarized in Table III, all the model diamides derived from **1** are levorotatory at 435 and 589 nm in DMAc and in aqueous NaOH solutions. **3a–c** are also levorotatory but with smaller absolute values of their rotations. This behavior suggests that these three polyamides form no exclusive conformation in these solutions.

In DMAc, a similar correlation is also observed in the optical rotations of **3e** and **5e** and those of **3f** and **5f**. By contrast, the mean residue rotation ($[m]_D$) (aqueous NaOH) of **3e** and **3f** are –181 and +1115, respectively, which are quite different from the molar rotations ($[M]_D$) (aqueous NaOH) of **5e** and **5f**. The abnormal optical rotation of **3e** and **3f** in aqueous NaOH is attributed to an

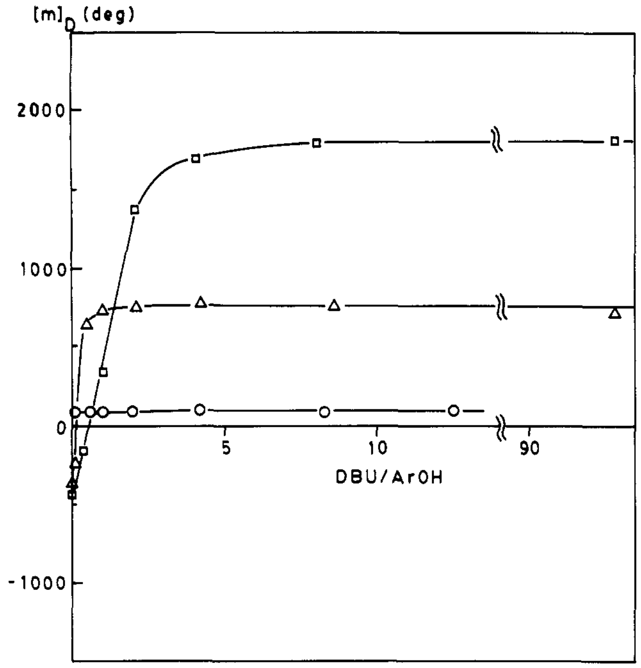


Figure 2. Changes of the mean residue rotation ($[m]^{21}{}_{D}$) of **3d–f** in DMAc with varying amounts of DBU: (○) **3d**; (□) **3e**; (△) **3f**.

ordered conformation of their polymer chains, which would result from the ionization of the phenolic hydroxyl groups in the side chains to phenolate anions. To substantiate this hypothesis, we measured $[m]_D$ (DMAc) of **3e** and **3f** containing various amounts of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which can transform the phenolic hydroxyl groups into phenolate anions. As shown in Figure 2, addition of a small amount of DBU caused a drastic change of $[m]_D$ of **3e** and **3f**. This result distinctly reflects the formation of an ordered conformation of **3e** and **3f** in aqueous NaOH and in DMAc with excess DBU.

Abnormal rotation was also observed for the $[m]$ (DMAc) of **3d**. But no information could be obtained for [**m**] (aqueous NaOH) of **3d** since unfortunately hydrolysis of the amide bonds easily occurred. This was thought to release the strain brought on by the repulsion of the phenolate anions in the very tight and rigid main chain. The $[m]$ (DMAc) of the shortened polyamide changed to negative and approached the reasonable value estimated on the basis of $[M]$ (DMAc) of **5d**. Moreover, the $[m]$ (DMAc) of **3d** is scarcely influenced by the addition of DBU as shown in Figure 2. These phenomena suggest that $[m]$ (DMAc) of **3d** includes a contribution of not only the optically active repeating unit but also of the polymer main chain. This decreases with a decrease in the degree of polymerization and does not change by converting the phenolic hydroxyl groups into phenolate anions.

CD Spectra. CD spectra of these polyamides in DMAc at wavelengths longer than 260 nm and in aqueous NaOH solution at wavelengths longer than 220 nm were compared with those of model diamides to elucidate the possible conformational changes of these polyamides.

The CD spectra of **3a–c** with those of the model diamides are shown in Figure 3. In DMAc, **5a** and **3a** show essentially the same CD spectra and exhibit a medium negative band at 275 nm, which may be assigned to a component of the split π–π^* transition of the hydroxyphenyl chromophore. In aqueous NaOH, the CD spectra of both **5a** and **3a** exhibit a marked enhancement of absorption and a bathochromic shift of 14 nm, which would result from the change of the chromophore from hydroxyphenyl to phenolate anion.

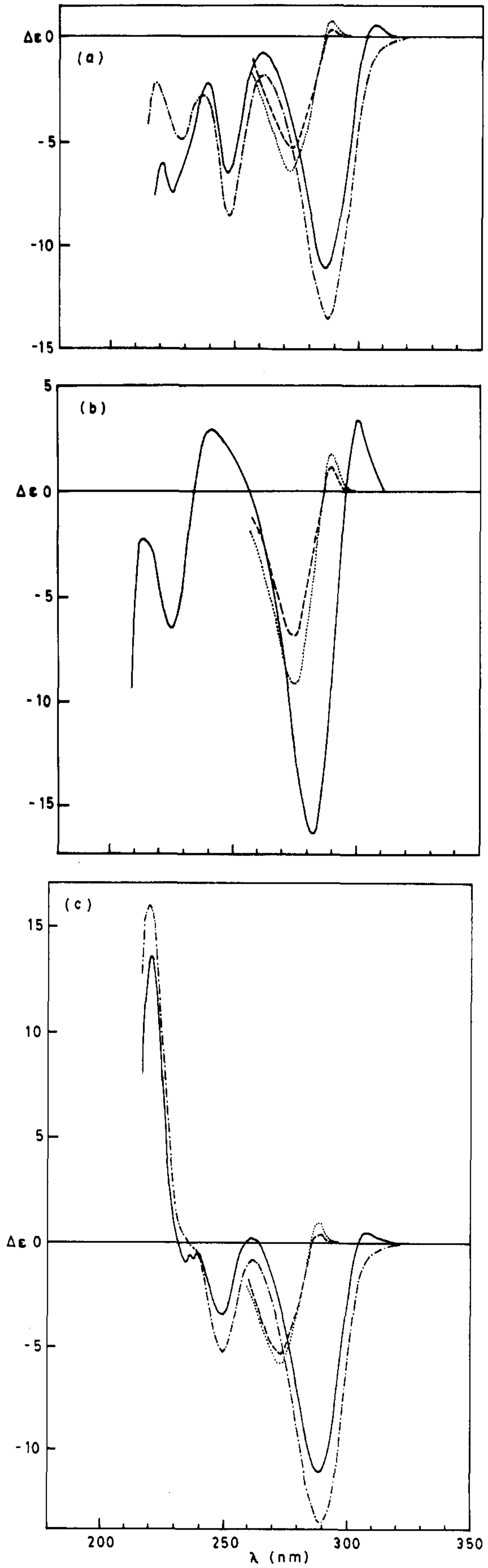


Figure 3. CD spectra of (a) **3a** and **5a**, (b) **3b** and **5b**, and (c) **3c** and **5c** in DMAc and 0.2 M aqueous NaOH: (---) **3** in DMAc; (···) **5** in DMAc; (—) **3** in aqueous NaOH; (-·-) **5** in aqueous NaOH. **5b** in aqueous NaOH is not included due to its insolubility.

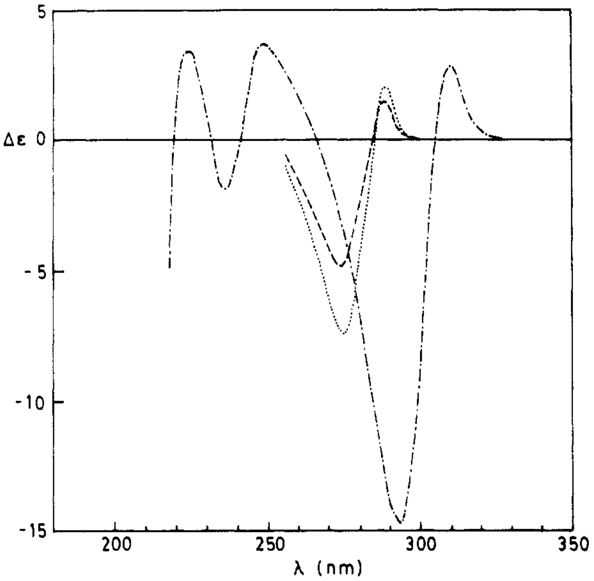


Figure 4. CD spectra of **3d** and **5d** in DMAc and 0.2 M aqueous NaOH: (---) **3d** in DMAc; (···) **5d** in DMAc; (-·-) **5d** in aqueous NaOH.

CD spectrum of **3c** is also essentially the same as that of corresponding model diamide **5c**.

The weaker Cotton effect of **3a** and **3c** compared to their model diamides in both DMAc and aqueous NaOH suggests that they exist in random conformation in these solutions.

In DMAc **3b** exhibits a medium negative band at 272 nm, which shifts only 9 nm to 281 nm in aqueous NaOH. The CD spectrum of **3b** in aqueous NaOH could not compared with that of **5b** since **5b** was insoluble in aqueous NaOH. Additionally, the negative band at about 250 nm in the CD spectrum of **3a** in aqueous NaOH was not observed in that of **3b**. But, **3b** would also exist in random conformation due to its flexible hexamethylene group similar to that in **3a**.

The CD spectra of **3d** and **5d** in DMAc are shown in Figure 4. The two spectra are quite similar except for their intensities, giving no valuable information as to the conformation of the polyamide. Moreover, we were unsuccessful in comparing the CD spectrum of **3d** in aqueous NaOH with that of the model diamide **5d** since the polyamide was easily hydrolyzed in aqueous NaOH. Then, we studied the CD spectrum of **3d** in DMAc with DBU on the basis of the fact that DMAc with excess DBU is a basic medium similar to aqueous NaOH. The CD spectrum of **3d** in DMAc remained almost the same by changing the ratio of DBU/ArOH from 0 to 10, indicating the firmly fixed structure of **3d**.

The CD spectra of **3e** and **3f** with those of their model diamides are shown in Figure 5. The much enhanced intensity of $\Delta\epsilon$ and ϵ compared to the other polyamides and diamides is due to the conjugation between the amide linkages and the aromatic moieties in the diamine or amine components. The CD spectrum of **5e** in DMAc exhibits a negative band at 278 nm, while that of **3e** exhibits a negative band at 282 nm, which is smaller than that of **5e** in intensity. In aqueous NaOH, the negative band of **5e** undergoes a bathochromic shift to 292 nm with a slight increase in intensity, but that of **3e** becomes significantly larger than that of **5e** with a similar bathochromic shift. Moreover, the pattern of the CD spectrum of **3e** in aqueous NaOH at wavelengths shorter than 270 nm is significantly different from that of the model diamide **5e**. These results indicate that **3e** exists in a random conformation in DMAc, but in aqueous NaOH it should form an ordered conformation. This explanation is consistent with the abnormal rotations of **3e** in aqueous NaOH mentioned above.

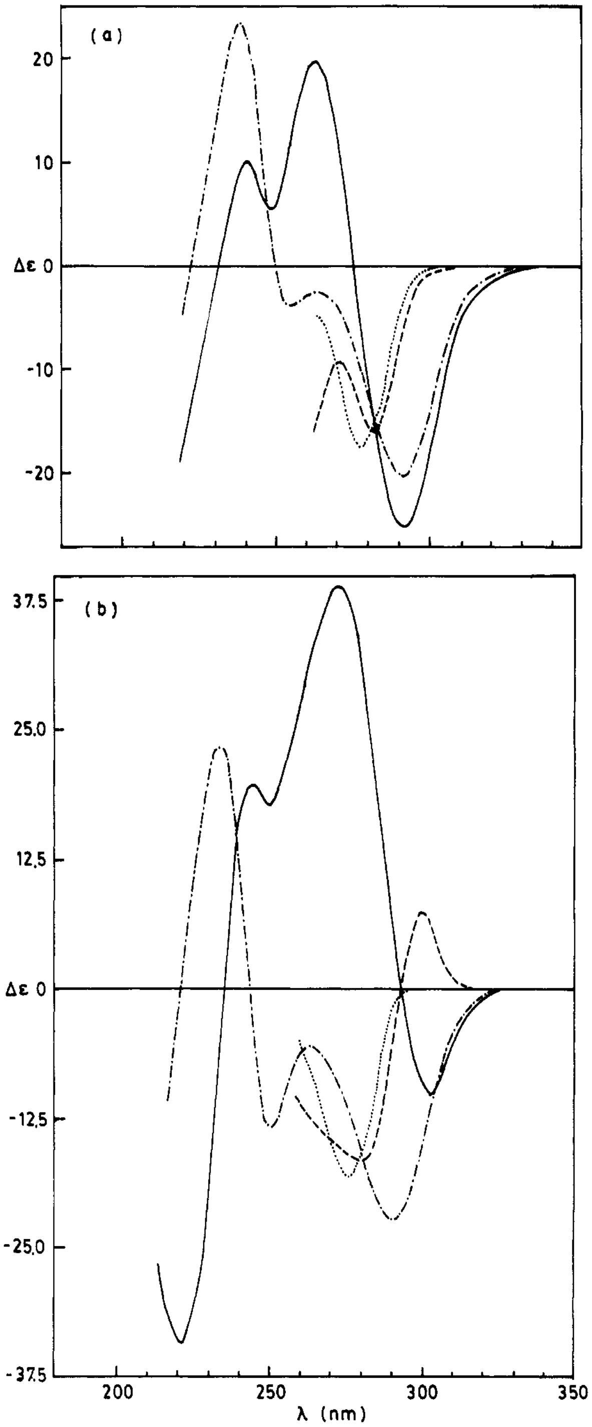


Figure 5. CD spectra of (a) **3e** and **5e**, and (b) **3f** and **5f** in DMAc and 0.2 M NaOH: (---) **3** in DMAc; (···) **5** in DMAc; (—) **3** in aqueous NaOH; (-·-) **5** in aqueous NaOH.

In aqueous NaOH solution, the CD spectrum of **3f** shows a medium negative band at 303 nm and a strong negative band at 275 nm, which is quite different from that of **5f** in aqueous NaOH, being almost the mirror image. Additionally, it exhibits a much stronger absorption than **5f** in aqueous NaOH, whereas both spectra show almost the same intensity in DMAc at about 281 nm. These CD spectral results suggest strongly that **3f** exists in an ordered conformation in aqueous NaOH.

In order to ascertain the existence of an ordered conformation of **3e** and **3f** in basic media, we measured their CD spectra on changing the concentration of DBU in

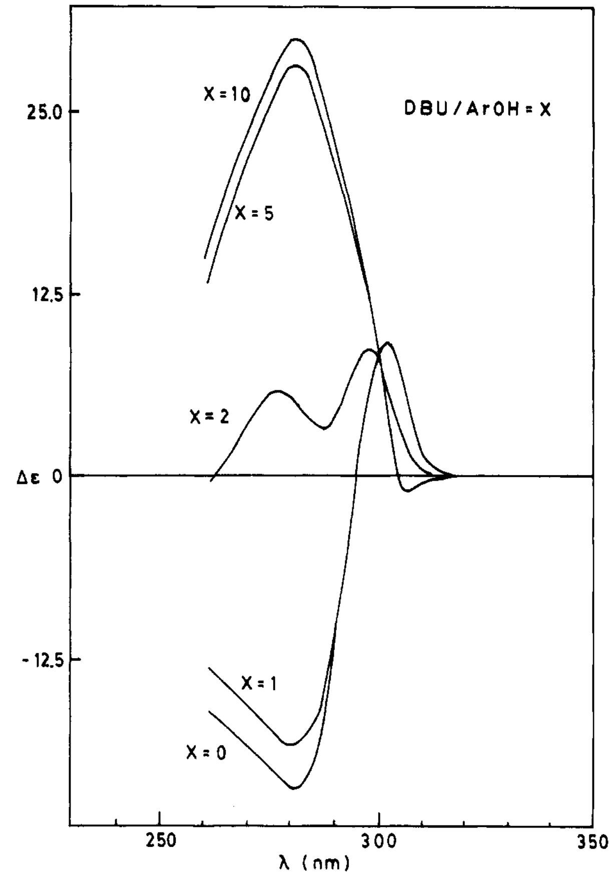


Figure 6. Changes in the CD spectra of **3f** in DMAc with varying amounts of DBU.

DMAc. As shown in Figure 6, the CD spectrum of **3f** exhibits a negative band at 281 nm in DMAc with DBU less than an equimolar amount of phenolic hydroxyl in the polyamide, but it changes drastically to a "positive" band at almost the same wavelength when the DBU/ArOH ratio is larger than 2. The CD spectrum at DBU/ArOH = 10 exhibits a much stronger intensity, which is almost the mirror image of that in DMAc. The latter is quite similar to that in aqueous NaOH. These phenomena strongly support that **3f** forms an ordered conformation both in aqueous NaOH and in DMAc with DBU, which acts as a strong base to transform phenolic hydroxyl groups to phenolate anions.

As shown in Figure 7, the CD spectrum of **3e** exhibits an increase in the intensity of the negative band at 280 nm by changing the DBU/ArOH ratio from 0 to 4, and the negative band decreases at higher DBU/ArOH ratios. At DBU/ArOH = 24, a strong positive band at 267 nm can be observed. These results suggest that **3e** forms at least a locally ordered conformation at DBU/ArOH ratios lower than 4 and then changes gradually into another ordered conformation at higher DBU/ArOH ratios.

These different optical rotation and CD spectral behaviors of optically active polyamides can be explained clearly in terms of the difference of rigidity of their backbone. The polymer main chains of **3a** and **3b** are considered to be too flexible to form an exclusive conformation. Moreover, the diacid components in the polymer main chain of **3c** are situated too far away to interact with each other and they can change their conformation rather easily in solution. This flexibility of the polymer main chain and/or isolation of the functional groups would lead to no structural contribution other than that of the repeating unit. **3e** and **3f** exist in firmly fixed conformations under basic conditions due to the repulsion of the phenolate anions. This arises because the rotation of the carbonyl carbon–cyclobutane carbon bond is restricted and/or the phenolate anion interacts with the amide to some extent. The backbone of **3d** seems too rigid and tight to take other than one fixed conformation regardless of medium.

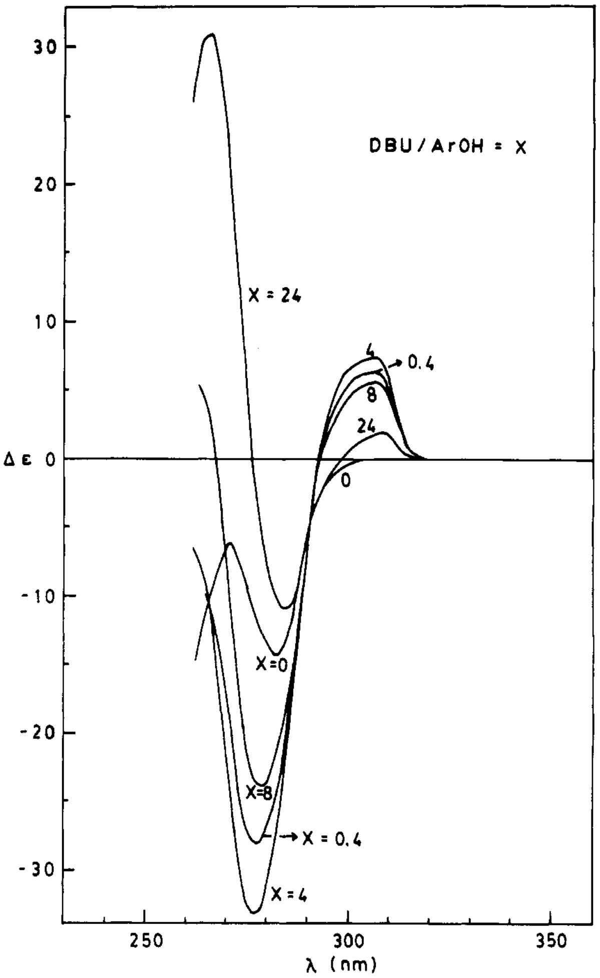


Figure 7. Changes in the CD spectra of **3e** in DMAc with varying amounts of DBU.

In fact, the Corey–Pauling–Koltun (CPK) space-filling molecular models of **3a–c** show that their polymer main chains are very flexible and can almost freely change conformations. The CPK models of **3e** and **3f** show that their polymer main chains are rather rigid but have sufficient distance between neighboring cyclobutane units to rotate around the carbonyl carbon–cyclobutane carbon bond. Then, they readily form an ordered conformation only in basic media, by the repulsion of phenolate anions. The CPK models of **3d** show that neither the polymer main chain nor the hydroxyphenyl group can rotate due to its very rigid structure.

Conclusion

High molecular weight optically active polyamides were easily obtained by the ring-opening polyaddition reaction of **1** with diamines.

The polyamides showed similar thermal behavior to their racemic counterparts and exhibit a decomposition temperature at ca. 250 °C in a nitrogen stream.

The drastic change of the CD spectrum of **3f** from a negative "Cotton effect" in DMAc to the mirror-imaged positive one in aqueous NaOH is attributed to the formation of an ordered conformation in aqueous NaOH, which is caused by the repulsion of the phenolate anions. Its CD spectral change in DMAc on addition of DBU is also consistent with the above explanation. **3e** also exists in an ordered conformation in aqueous NaOH on the basis of abnormal optical rotation and CD spectrum. **3e** and **3f** would be new polyamides exhibiting reversible formation of a ordered conformation on changing the basicity of the media.[15] Although the CD spectra of **3d** in DMAc and in aqueous NaOH are not conclusive, **3d** would exist in a very rigid and tight structure that cannot be altered by the basicity of the media.

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Monte Carlo Simulation Study of the Polymerization of Polyurethane Block Copolymers. 1. Natural Compositional Heterogeneity under Ideal Polymerization Conditions

Thomas A. Speckhard,[†] John A. Miller,[†] and Stuart L. Cooper*

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706.
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ABSTRACT: The synthesis of polyurethane block copolymers is a complex process involving the condensation polymerization of three monomers in a one-step, two-step, or multistep reaction with the composition and molecular weight distributions of the final polymer influenced by a number of factors including the extent of reaction; relative reactivity, type, and amount of the monomers; and the extent to which various side reactions occur. In order to describe the effects of various reaction parameters on the composition and molecular weight distributions of polyurethane block copolymers, a Monte Carlo simulation has been developed utilizing several simplifying assumptions proposed by Peebles (Peebles, L. H. *Macromolecules* 1974, *7*, 872). The model calculates the molecular weight and composition distributions of the final polymer and simulates fractionation of the polymer based on composition. Using this idealized model, the effects of varying the average degree of polymerization, diisocyanate reactivity ratio, hard-segment content, soft-segment molecular weight distribution, average hard- and soft-segment block length, hard-segment type, and lower limit of the degree of polymerization on the composition and molecular weight distributions of polyurethane block copolymers are determined and discussed.

I. Introduction

Polyurethane block copolymers are usually prepared in a two-step reaction by first reacting a diisocyanate with a hydroxy-terminated polyether or polyester macroglycol. This oligomer is commonly referred to as the soft-segment polyol. The diisocyanate groups are in excess; therefore, the primary product of the first step of the reaction is a diisocyanate-capped soft segment. The reaction products will also include unreacted diisocyanate molecules and some higher molecular weight species produced by linking two or more soft segments through reaction of both ends of a diisocyanate molecule. It is generally assumed that all of the soft-segment hydroxyl groups react, and therefore all product species are isocyanate terminated.[1]

In the second reaction step, the remaining isocyanate functionality is then reacted with a low molecular weight diol or diamine, which is known as the chain extender. Reaction of the chain extender with the free diisocyanate molecules produces hard-segment sequences of various lengths with the average length depending on the stoichiometry of the overall reaction. In the final polymer, the hard and soft segments tend to segregate, due to their incompatibility, and produce a phase-separated morphology of hard-segment-rich and soft-segment-rich phases. This two-phase structure gives rise to the interesting and useful properties of these materials.[2,3]

Normally, the amount of chain extender added in the second step is such that in the final reaction mixture there are an equal number of hydroxyl and isocyanate groups. In some cases, excess isocyanate functionality is used to promote cross-linking by the reaction of active urethane hydrogen atoms (or urea hydrogens if a diamine chain extender is used) to form allophanate (or biuret) linkages. Excess isocyanate is also used because any water present in the system will react with the isocyanate groups, leading to a lower molecular weight in water-poisoned systems that are stoichiometric. The reaction chemistry is further complicated by the fact that the isocyanate groups can

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[†] Current address: 3M Research Center, St. Paul, MN 55144.

* Author to whom correspondence should be addressed.

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