Structural Isomerism in Polycondensates. 5. Configurational Characteristics of the Amide Groups in Some N-Methylated Polyamides of Different Isomeric Structure

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ABSTRACT: The influence of polymer constitution on the configurational preferences of the amide groups in polyamides formed by nonsymmetric (–ab–) methylimino(1,4-phenylene)ethylenemethylimino units and symmetric (–cc–) carbonyltetramethylenecarbonyl units has been investigated. The study has been performed by using isomeric polyamides with head-to-tail, head-to-head/tail-to-tail, and nearly random constitution and model diamides containing the –acca–, –bccb–, or –accb– sequence. The polymers and the model compounds have been analyzed by solution ^{1}H NMR techniques. The results confirm that the N-methylated amide groups can assume both configurations and reveal differences in the configurational preferences of the different groups under the experimental conditions used. Thus, while the –ca– groups ($-CH_2CH_2CON(CH_3)$-*p*-C_6H_4-) have a very strong tendency to adopt the *E*-configuration, the –bc– groups ($-CH_2CH_2N(CH_3)COCH_2CH_2-$) prefer the *Z*-configuration, the preference being stronger in the polymers than in the model compounds. The results also indicate that, at least with solvents such as *o*-dichlorobenzene or chloroform, the preference of the –bc– groups of the polyamides for the *Z*-configuration depends to some extent on the polymer constitution.

Introduction

For studies of the influence of constitutional isomerism on the physical properties of polycondensates,[1-4] unsubstituted polyamides and polyureas may not be very suitable because strong effects brought about by extensive interchain NH···OC bonds may mask subtle effects due to isomerism. N-Substituted polyamides and polyureas, which cannot form these bonds, may provide more convenient systems for these kinds of studies. As an extension of earlier investigations,[1,2] we have synthesized and studied a group of isomeric N-methylated polyamides with chains formed by nonsymmetric (–ab–) methylimino(1,4-phenylene)ethylenemethylimino and by symmetric (–cc–) carbonyltetramethylenecarbonyl units (Chart I). The polymers were ordered, with a head-to-tail (PI) or head-to-head/tail-to-tail (PII) constitution, or unordered (PIII). An interesting possibility suggested for these polyamides by several studies[5-8] was that the *E*- and *Z*-configurations of the N-methylated amide groups (–ac– and –bc–; Chart II) could both occur in solutions. In this case, possible influences of the polymer constitution on the relative population of *E*- and *Z*-isomers can be observed. In this work we have explored this possibility by using the three model diamides MI, MII, and MIII (Chart I), which contain the sequences [–acca–, –bccb–, and –accb–] occurring in the polyamides investigated.

Experimental Section

Materials. All reagents and solvents were commercial products of the highest quality available and were used, in general, as received. 4-Ethylaniline, *N*-methyl-*N*-(2-phenylethyl)-amine, and adipic acid dichloride were purified by distillation under reduced pressure before use. 2-(4-Aminophenyl)ethylamine was refluxed over CaH_2 for 2 h and then distilled. Pyridine was refluxed over KOH under nitrogen and then distilled. Triethylamine (TEA) was purified first by refluxing with benzoyl chloride and distilling. The final purification was done by refluxing over CaH_2 and distilling again.

Syntheses. A. Model Diamides. *N,N'*-Dimethyl-*N,N'*-bis(4-ethylphenyl)adipamide (MI), *N,N'*-dimethyl-*N,N'*-bis(2-phenylethyl)adipamide (MII), and *N,N'*-dimethyl-*N*-(4-ethylphenyl)-*N'*-(2-phenylethyl)adipamide (MIII) were synthesized as shown in Scheme I.

MI. For the preparation of *N*-methyl-4-ethylaniline (**2**) the method used by Johnstone and others[9] was followed. 4-Ethyltrifluoroacetanilide (**1**, obtained and purified as described in the literature[10]) was N-methylated and the N-methylated product was hydrolyzed without isolation. **2** was purified by distillation under reduced pressure: bp 130 °C (35 mmHg); n^{20}_D 1.6820; yield, 83%. Elem anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.68; H, 9.83; N, 10.38. ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.97, 6.47 (4 H, m, 4 ArH), 3.36 (1 H, br, NH), 2.69 (3 H, s, CH_3N), 2.32 (2 H, q, CH_3CH_2, J = 8 Hz), 1.17 (3 H, t, CH_3CH_2, J = 8 Hz).

The reaction of **2** with adipic acid dichloride to obtain MI was carried out using dioxane as the solvent and pyridine as the base. The crude diamide was purified by recrystallization from ether: mp 67.1 °C; yield, 90%. Elem anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.79; H, 8.66; N, 7.53.

MII. The reaction of *N*-methyl-*N*-(2-phenylethyl)amine with adipic acid dichloride was carried out with ether as the solvent and triethylamine as the base. The crude product was purified by recrystallization from ether: mp 48.0 °C, yield, 40%.

Elem anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.73; H, 8.63; N, 7.38.

MIII. *N*-Methyl-*N*-(2-phenylethyl)adipamic acid (**3**) was obtained by letting *N*-methyl-*N*-(2-phenylethyl)amine react with adipic acid anhydride[11] in CH_2Cl_2 at −50 °C for 1 h. **3** was obtained as a colorless liquid upon evaporation of the solvent and was purified by crystallization from ether: mp 91.3 °C; yield, 69%. Elem anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.24; H, 8.04; N, 5.32. Found: C, 68.26; H, 7.94; N, 5.39. ^{1}H NMR (60 MHz, $CDCl_3$): δ 11.1 (1 H, s, COOH), 7.23 (5 H, m, ArH), 3.50 (2 H, m, CH_2N), 2.95, 2.85 (3 H, s, CH_3N), 2.80 (2 H, m, $ArCH_2$), 2.30 (4 H, m, CH_2CO), 1.65 (4 H, m, CH_2CH_2CO).

N,N'-Dicyclohexylcarbodiimide (DCC) (0.92 g, 4.5 mmol) was added to a cold (−8 °C) solution of **2** (0.49 g, 3.6 mmol) and **3** (0.95 g, 3.6 mmol) in CH_2Cl_2 (30 mL), and the mixture was kept under stirring for 20 h. The precipitate formed was filtered off, the filtrate was evaporated, and the residue was dissolved in ethyl acetate. This solution was washed with aqueous solutions of citric acid and of $NaHCO_3$, in that order, and then with water and finally dried. The crude product was obtained upon evaporation of the solvent as a slightly yellow liquid and was purified by column chromatography on silica

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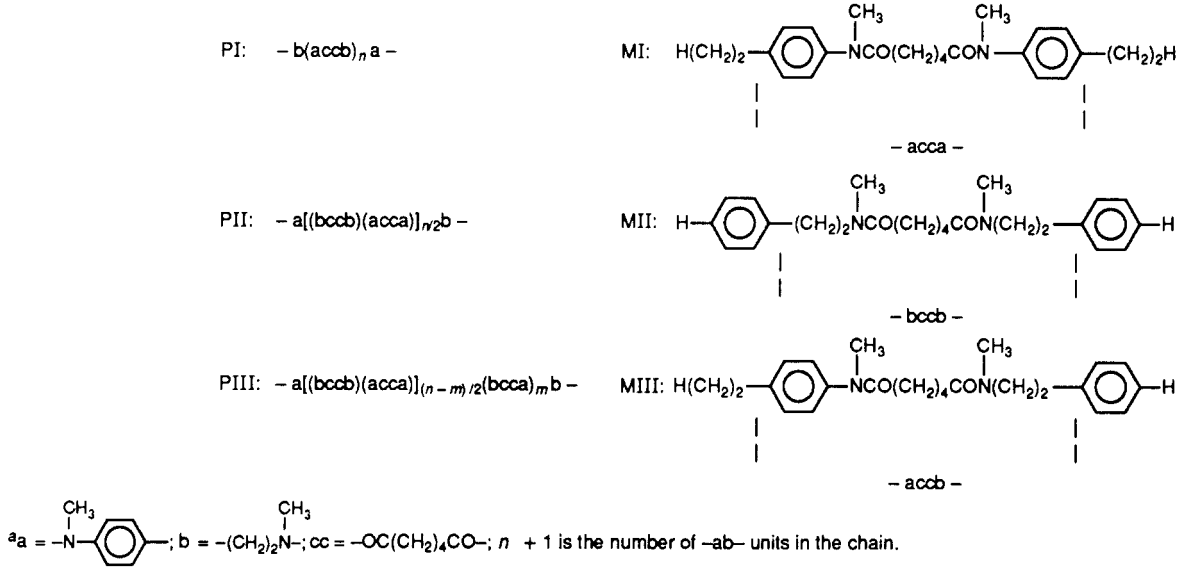
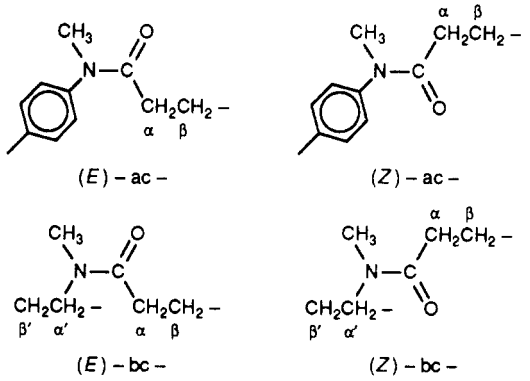
Chart I[a]
Schematic Formulas of the Polyamides (PI, PII, and PIII) and Formulas of the Three Model Diamides Studied

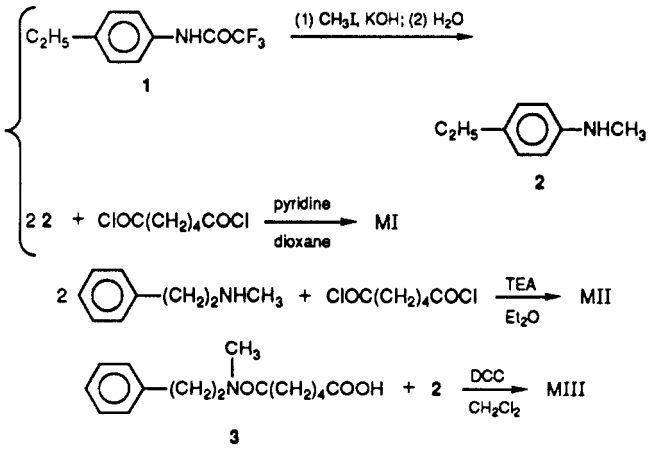


[a] a = –N(CH$_3$)–C$_6$H$_4$–; b = –(CH$_2$)$_2$N(CH$_3$)–; cc = –OC(CH$_2$)$_4$CO–; n + 1 is the number of –ab– units in the chain.

Chart II
Configurations of the Two Kinds of Amide Groups –ac– and –bc– Present in the Model Diamides and in the Polyamides



Scheme I
Syntheses of the Model Diamides



gel (eluent, acetone) and subsequent crystallization (i-Pr$_2$O/n-hexane): mp 46.4 °C; yield, 0.58 g (43%). Elem anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.05; H, 8.35; N, 7.31.

B. Polyamides. Monomers. *N*-Methyl-*N*-[2-[4-(methylamino)phenyl]ethyl]adipamic Acid (4). This monomer was obtained by reaction of *N*-methyl-[2-[4-(methylamino)phenyl]-ethyl]amine with an equimolar amount of adipic acid anhydride[11] in dimethylformamide at room temperature. The crude product was purified by column chromatography (silica gel; eluent, EtOH/CHCl$_3$ (2/8 by volume) and was obtained as a slightly yellow oil with a 72% yield. ^{1}H NMR (CDCl$_3$): δ 6.96, 6.88 (2 H, m, ArH), 6.86 (1 H, br, NH), 6.51 (2 H, m, ArH), 3.46, 3.37 (2 H, m, CH$_2$N), 2.88, 2.80 (3 H, s, CH$_3$NCO), 2.74, 2.73 (3 H, s, CH$_3$NAr), 2.65 (2 H, m, ArCH$_2$), 2.31–1.96 (4 H, m, CH$_2$CO), 1.59, 1.45 (4 H, m, *CH*$_2$CH$_2$CO).

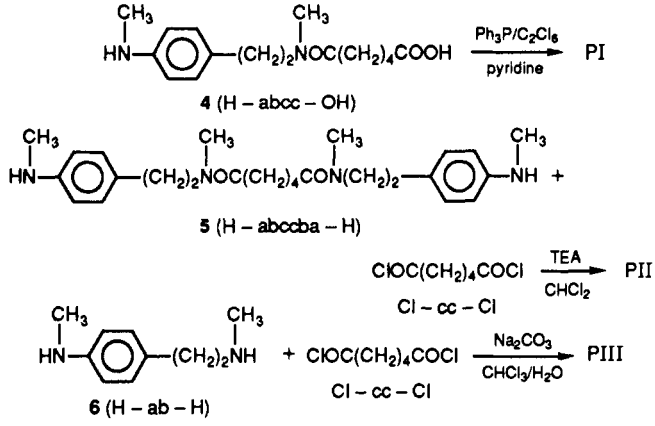
***N*,*N*′-Dimethyl-*N*,*N*′-bis[2-[4-(methylamino)phenyl]-ethyl]adipamide (5).** This monomer was obtained by reaction of **6** (see below) with bis(*p*-nitrophenyl adipate) [mp 122.6 °C (lit.[12] mp 123–4 °C; obtained by the reaction of adipic acid dichloride with *p*-nitrophenol in ether, in the presence of triethylamine)] by using a 2/1 molar ratio of amine to ester and a 1/1 (by volume) CH$_2$Cl$_2$/acetone mixture as the solvent. **5** was purified by repeated recrystallizations from Et$_2$O and from CH$_2$Cl$_2$/Et$_2$O: mp 133.4 °C; yield 66%. Elem anal. Calcd for $C_{26}H_{38}N_4O_2$: C, 71.20; H, 8.73; N, 12.77. Found: C, 70.46; H, 8.67; N, 12.52. ^{1}H NMR (ODCB-d_4, 120 °C): δ 6.91, 6.42 (8 H, m, ArH), 3.46 (4 H, t, CH$_2$N), 3.35 (2 H, br, NH), 2.82 (6 H, s, CH$_3$NAr), 2.66 (10 H, m, CH$_3$NCO + ArCH$_2$), 2.17 (4 H, m, CH$_2$CO), 1.66 (4 H, m, *CH*$_2$CH$_2$CO).

***N*-Methyl-2-[4-(methylamino)phenyl]ethylamine (6).** This monomer was obtained by converting first 2-(4-aminophenyl)-ethylamine into its di-Boc derivative, N-methylating this derivative, and finally removing the Boc groups from the dimethylated product. The di-Boc derivative was synthesized by the di-*tert*-butyl dicarbonate method[13] and purified by recrystallization from EtOH/H$_2$O, mp 151.5 °C. The N-methylation was performed following Olsen's procedure,[14] and the liquid product was purified by distillation under reduced pressure: bp 155–160 °C (0.025 mmHg) n^{20}_D = 1.4948. The deprotection was performed by using trifluoroacetic acid. The crude **6** was purified by distillation: bp 101–102 °C (0.13 mmHg). ^{1}H NMR (90 MHz, CDCl$_3$): δ 7.05, 6.58 (4 H, m, ArH), 3.60 (1 H, br, ArNH), 2.82 (3 H, s, ArNCH$_3$), 2.91–2.71 (4 H, m, CH$_2$), 2.43 (3 H, s, *CH*$_3$NHCH$_2$), 1.50 (1 H, br, N*H*CH$_2$).

Polycondensation Reactions. PI. **4** (0.178 g, 0.6 mmol) and Ph$_3$P (0.19 g, 0.72 mmol) were dissolved in pyridine (1.5 mL), and hexachloroethane (0.21 g, 0.90 mmol) was added. The mixture was stirred for 2 h at room temperature, and the solvent was evaporated. The crude polymer obtained was purified by precipitation from CH$_2$Cl$_2$ with *n*-hexane and washing with H$_2$O and then with ether: yield, 0.115 g (70%); [η] = 0.40 dL/g.

PII. A cold (0 °C) solution of adipic acid dichloride (0.766 g, 4.19 mmol) in 9 mL of CHCl$_3$ was mixed under stirring with a cold (0 °C) solution of **5** (1.837 g, 4.19 mmol) in 10 mL of CHCl$_3$ and CH$_2$Cl$_2$ (1/1 by volume), and then 3.2 g (23 mmol) of triethylamine was added. The homogeneous reaction mixture was stirred overnight at room temperature; it was then diluted with additional CHCl$_3$ and washed with H$_2$O several

Scheme II
Polycondensation Reactions Used for the Synthesis of the Polyamides



times. The polyamide obtained was isolated by evaporation of the solvents and purified by precipitation from a CH_2Cl_2 solution with *n*-hexane: yield, 2.00 g (87%); $[\eta]$ = 0.61 dL/g.

PIII. To a cold (0 °C) solution of **6** (1.480 g, 9.01 mmol) and Na_2CO_3 (1.912 g, 18.0 mmol) in 90 mL of H_2O in a Waring blender was rapidly added with a syringe while vigorously stirring a solution of adipic acid dichloride (1.650 g, 9.01 mmol) in 9 mL of $CHCl_3$. The mixture was stirred for 10 min. Then, the polyamide was extracted with $CHCl_3$, isolated by evaporation of the solvent, and purified by precipitation from a CH_2Cl_2 solution with *n*-hexane: yield, 2.23 g (90%); $[\eta]$ = 0.52 dL/g.

Methods. The elemental analyses were done by the microanalytical laboratory of the Organic Chemistry Institute of the ETH, Zürich, and by the analytical laboratory of Ciba-Geigy Ltd., Basel, Switzerland.

NMR. Except otherwise indicated in the text, the spectra were measured on a Bruker AM-300-WB spectrometer. The solution concentration for the ^1H NMR spectra was in all cases in the range 8–40 mg/mL and for the ^{13}C NMR spectra in the range 40–100 mg/mL. All chemical shifts are relative to internal tetramethylsilane. Nuclear Overhauser enhancement (NOE) effects were evaluated using one-dimensional NOE difference experiments. For the quantitative configurational analysis the intensities of appropriate signals in the ^1H NMR spectra were used. In the case of PI the $[Z]/[E]$ ratio was calculated as $5I_z/(2I_{total} - 5I_z)$, I_{total} being the total area of the signals contributed by the $CH_2(\alpha')$ protons and by the protons of the NCH_3 group of –ac– segments (Figure 3) and I_z the area of the signal given by $CH_2(\alpha')$ protons of –bc– segments in the *Z*-configuration. The area of this signal was measured by taking the minimum of the curve (at 3.42 ppm in Figure 3) as the highest field limit of the signal. In the case of PII and PIII the calculation of the $[Z]/[E]$ ratio was done on the basis only of the two signals given by the $CH_2(\alpha')$ protons (Figure 3).

The activation energies for the $Z \rightarrow E$ isomerization (Table IV) were calculated from the coalescence temperatures of the appropriate singlets given by NCH_3 protons taking into due account the different intensity of the signals.[15,16]

Molecular weights were determined by vapor pressure osmometry at 25 °C with $CHCl_3$ as solvent using a Wescan Model 232 A instrument.

Glass transition temperatures were obtained by differential thermal analysis (DTA). Intrinsic viscosities were determined at 25 °C using $CHCl_3$ as solvent.

Results and Discussion

A. Synthesis and Constitution of the Polymers. Different synthetic pathways (Scheme II) were followed to obtain the isomeric N-methylated polyamides PI, PII, and PIII. The head-to-tail polyamide PI, with the nonsymmetric units –ab– all equally oriented, was obtained by polycondensation of *N*-methyl-*N*-[2-[4-(methylamino)phenyl]ethyl]adipamic acid (**4**). The polycondensation was carried out by the method of Wu et al.[17,18] The

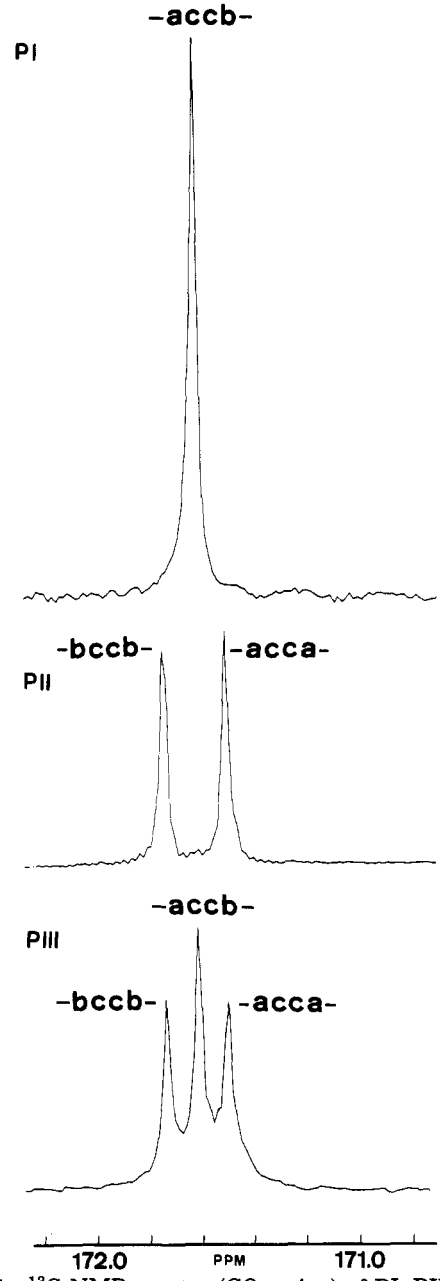


Figure 1. ^{13}C NMR spectra (CO region) of PI, PII, and PIII in DMSO-d_6 at 120 °C. The assignment is based on the comparison with spectra of the model diamides.

head-to-head/tail-to-tail polyamide PII, with alternating orientation of the nonsymmetric units, was obtained by solution polycondensation of *N*,*N*′-dimethyl-*N*,*N*′-bis[2-[4-(methylamino)phenyl]ethyl]adipamide (**5**) with adipic acid dichloride. ^{13}C NMR spectra of these polymers (solvent, DMSO-d_6; *T*, 120 °C), which exhibited a single nonresolved CO signal in the case of PI (the model MIII of this polyamide shows two signals separated by only 0.08 ppm) and two CO signals of equal intensity in the case of PII (Figure 1), confirmed their structure and indicated that no substantial transamidation had taken place during the polycondensation. The unordered polyamide PIII was obtained from *N*-methyl-2-[4-(methylamino)phenyl]ethylamine (**6**) and adipic acid dichloride by interfacial polycondensation. ^{13}C NMR spectra of this polyamide showed three CO signals (Figure 1) with intensities in the approximate ratio 2.7:4.5:2.7 corresponding to a value of s^{19} (0.45) near to that expected for a strictly random polymer (0.50). Some characteristics of the polyamides are reported in Table I. In contrast to the related,

Table I
Characteristics of the Polyamides

polyamide	$\bar{M}_n$	s^a	$[Z]/[E]^b$	T_g, °C	solubility,^{c} g
PI	2000	1	1.56[d]	46	0.23
PII	3200	0	1.50[e]	49	0.56
PIII	2900	0.45	1.56[e]	51	0.61

[a] [-accb-]/([-acca-] + [-accb-] + [-bccb-]).[19] [b] Ratio of the concentrations of -bc- groups in the *Z*- and *E*-configuration at 25 °C and with ODCB-d_4 as solvent. [c] Volume fraction of H_2O to be added to develop turbidity in a polymer solution containing 1 g of polymer/g of EtOH (*T*, 30 °C). Determined by turbidimetric titration.[20] [d] Estimated error ±5%. [e] Estimated error ±2%.

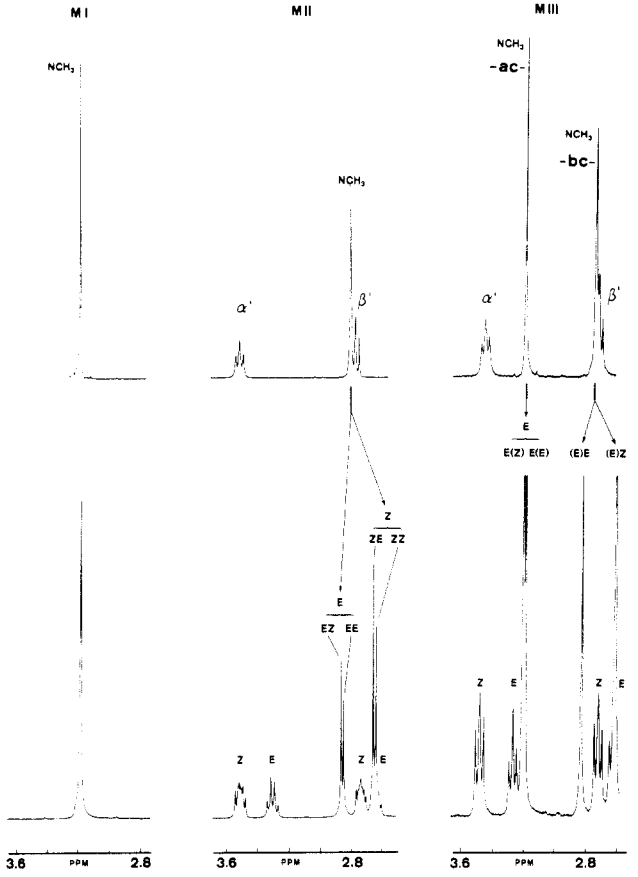


Figure 2. Partial ^{1}H NMR spectra of the diamides in ODCB-d_4 showing the region of the NCH_3, $CH_2(\alpha')$, and $CH_2(\beta')$ signals: top, 120 °C; bottom, 25 °C. The arrows indicate the splitting of the NCH_3 signals, which takes place on lowering the solution temperature.

nonmethylated polymer (mp 312 °C),[21] these N-methylated polyamides do not crystallize. The polyamides are all very soluble in many solvents, but differences in solubility do exist (Table I).

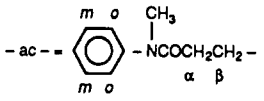
B. Configurational Isomerism. Model Diamides. The configurational analysis of MI, MII, and MIII was carried out by ^{1}H NMR using deuterated *o*-dichlorobenzene (ODCB-d_4), dimethyl sulfoxide (DMSO-d_6), $CDCl_3$, and other solvents at different temperatures. At 120 °C, in the first two solvents, the diamides give simple spectra (Figure 2, upper series) with signals that can be easily assigned on the basis of their relative intensity, of their multiplicity, and of their spectral position. At more moderate temperatures MI in $CDCl_3$ and MII and MIII in all solvents used give spectra showing different sets of signals thus revealing the presence in solution of different diastereoisomers. In the following we discuss separately the configurational assignment of the signals for spectra given by these diamides in ODCB-d_4 solution at 25 °C (Figure 2, lower series). The spectral position of these signals and the assignment done are indicated in Tables II and III. The assignment with other solvents was done by using similar criteria.

MI. No splitting of signals is observable with ODCB-d_4 when the solution temperature is lowered from 120 to 25 °C. Since there is always a unique set of signals, there can be only a species for MI in solution and this must be either the *EE*- or *ZZ*-diastereoisomer. A significant (6%) NOE effect was observed between the $CH_2(\alpha)$ and the ortho protons showing (compare Chart II) that the diastereoisomer present is the *EE* one.

MII. In spectra of solutions of this diamide in ODCB-d_4 at 25 °C there are four singlets given by NCH_3 protons, indicating that the three diastereoisomers *EE* (1 NCH_3 singlet), *EZ* (2 NCH_3 singlets of equal intensities), and *ZZ* (1 NCH_3 singlet) possible for this diamide are all present. These singlets form two close pairs of which the low-field one can be associated with amide groups in the *E*-configuration and the high-field one with amide groups in the *Z*-configuration. This conclusion is based both on results of NOE measurements and on observations regarding the solvent dependence of the chemical shifts.[22-24] In fact, NOE measurements have shown that only the NCH_3 singlets of the high-field pair give significant effects with signals (not shown in Figure 2) of the $CH_2(\alpha)$ protons (see Chart II), and the study of solvent effects has indicated that this high-field pair moves markedly more downfield than the low-field pair (0.35 against 0.15 ppm) when replacing the solvent ODCB-d_4 with $CDCl_3$. The assignment of the individual NCH_3 singlets has been done by using the signal intensities as measured in the spectrum shown (Figure 2) and in other spectra with less overlapping. The assignments of the other signals are based on the observation of other NOE effects, correlating the $CH_2(\alpha)$ and $CH_2(\alpha')$ multiplets given by amide -bc- groups in the *E*-configuration (Chart II), and on results of spin decoupling.

MIII. As shown in Figure 2, spectra of solutions of this diamide in ODCB-d_4 at 25 °C exhibit four NCH_3 signals, two of them (very close to each other) being given by the -ac- groups and the other two by the -bc- groups. These signals have been assigned specifically as indicated in Figure 2 and in Tables II and III on the basis of analogies in spectral position with MI and MII and of signal intensities. The spectra reveal that MIII occurs essentially in two diastereoisomeric forms only, one with both amide groups in the *E*-configuration and the other with the -ac- group in *E*-configuration and the -bc- group in the *Z*-configuration. Quantitative data regarding the configurational equilibrium at 25 °C of the three diamides have been calculated from the intensities of pertinent signals assigned as discussed above and are reported in Table IV. The data show that the -ac- groups, which have been found to have the configuration *E* in crystals of MI,[25] have a very strong tendency to stay in this configuration in solution. This result is in keeping with earlier observations for *N*-methylacetanilide.[26,27] In contrast, the -bc- groups prefer the *Z*-configuration. The equilibrium distribution depends on the solvent. As shown in Table IV, in the case of MII the ratio [*EZ*]/[*EE*] is nearly 4 times the ratio [*ZZ*]/[*EZ*] in the mixed solvent $CDCl_3/C_6D_6$, but it is significantly less than that in the other solvents. It is evident that the two amide groups, which in the diamide are separated by four methylene groups, do not behave independently. Apparently the energy associated with a -bc- group of MII in the *Z*-configuration is smaller in a *ZZ*- than in a *ZE*-diastereoisomer or that associated with a -bc- group in the *E*-con-

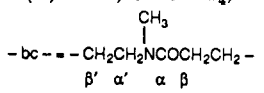
Table II
Chemical Shifts of the Protons of the -ac- Groups in MI, in MIII, and in the Polyamides and Configurational Assignment (*T*, 25 °C; ODCB-d_4)



amide	sequence type	signal position: *o*	*m*	NCH_3	α	β	sequence configuration[a]	population[b]
MI	-acca-	6.93	7.07	3.18	2.00	1.55	*EE*	100
MIII	-accb-	6.96[c]	7.07[c]	3.20	1.90	1.58[c]	*E*(*E*)	43
		6.96[c]	7.07[c]	3.22	2.03	1.58[c]	*E*(*Z*)	57
PI	-accb-	7.01[c]	7.11[c]	3.22[c]	1.96	1.58[c]	*E*(*E*)	39
		7.01[c]	7.11[c]	3.22[c]	2.10	1.58[c]	*E*(*Z*)	61
PII	-acca-	6.97	7.11	3.19	2.03	1.57	*EE*	100
PIII	-acca-	6.98[c]	7.12[c]	3.19	2.07[c]	1.56[c]	*EE*	100
	-accb-	6.98[c]	7.12[c]	3.20	2.07[c]	1.56[c]	*E*(*E*)	*d*
		6.98[c]	7.12[c]	3.22	2.09[c]	1.56[c]	*E*(*Z*)	*d*

[a] The configuration in parentheses is that assigned to the amide group -bc-. [b] Percent of the sequences of the type specific having the configuration indicated in the penultimate column. [c] Different overlapping signals. The position is that of the highest intensity peak. [d] Not determinable because of overlapping.

Table III
Chemical Shifts of the Protons of the -bc- Groups in MII, in MIII, and in the Polyamides and Configurational Assignment (*T*, 25 °C; ODCB-d_4)



amide	sequence type	signal position: β'	α'	NCH_3	α	β	sequence configuration[a]	population[b]
MII	-bccb-	*d*	3.03	2.85	1.96	1.50	*EE*	18
		d	3.32	2.87	2.00	1.58[c]	*EZ*[e]	47
		2.75[c]	3.49	2.65	2.08	1.58[c]	*EZ*[f]	
		2.75[c]	3.52	2.67	2.15	1.66	*ZZ*	35
MIII	-accb-	2.61	3.26	2.83	2.03	1.58[c]	(*E*)*E*	43
		2.72	3.48	2.61	2.09	1.58[c]	(*E*)*Z*	57
PI	-accb-	2.71[c]	3.34	2.86	2.10[c]	1.58[c]	(*E*)*E*	39
		2.71[c]	3.51	2.71	2.10[c]	1.58[c]	(*E*)*Z*	61
PII	-bccb-	2.72[c]	3.38[c]	2.89	2.03[c]	1.57	*EE*	*d*
		2.72[c]	3.38[c]	2.90	2.03[c]	1.63	*EZ*[e]	*d*
		2.72[c]	3.54[c]	2.76[c]	2.21[c]	1.63	*EZ*[f]	
		2.72[c]	3.54[c]	2.76[c]	2.21[c]	1.70	*ZZ*	
PIII	-accb-	*d*	3.36[c]	2.86	2.07[c]	1.56[c]	(*E*)*E*	*d*
		d	3.51[c]	2.71	2.09[c]	1.56[c]	(*E*)*Z*	*d*
	-bccb-	*d*	3.36[c]	2.88	2.07[c]	1.56[c]	*EE*	*d*
		d	3.36[c]	2.90	2.07[c]	1.62[c]	*EZ*	*d*
		d	3.51[c]	2.76	2.09[c]	1.62[c]	*Z*[g]	*d*

[a] The configuration in parentheses is that assigned to the amide group -ac-. [b] Percent of the sequences of the type specified having the configuration indicated in the penultimate column. [c] Different overlapping signals. The position is that of the highest intensity peak. [d] Not determinable because of overlapping. [e] The signals with the indicated position are assigned to the -bc- group in the *E*-configuration. [f] The signals with the indicated position are assigned to the -bc- group in the *Z*-configuration. [g] In *EZ* and *ZZ* sequences.

figuration is higher in an *EE*- than in an *EZ*-diastereoisomer. Table IV also shows that the configurational distribution ([*Z*]/[*E*]) of the -bc- groups in MII is significantly different from that in MIII with both ODCB-d_4 and $CDCl_3$ as the solvent. This is an important result since it implies that these groups must also behave differently in the sequences -accb- (PI and PIII) and -bccb- (PII and PIII) of the polyamides investigated.

Polyamides. Like the model diamides, at 120 °C in ODCB-d_4 (Figure 3, upper series) or DMSO-d_6, PI, PII, and PIII give simple ^1H NMR spectra. The signals of these spectra can be easily assigned on the basis of the positional analogies existing with corresponding signals of the model compounds. Similar to the case of the model diamides, also for the polyamides there is a splitting of the various NMR signals taking place on lowering the solution temperature, thus showing that there are amide groups occurring in different configurations. This splitting leads to complicated spectra with severe overlappings (Figure 3, lower series). A configurational analysis is still possible, however, if the very reasonable assumption is made that the relative spectral position of signals associated with different configurations corresponds to that observed for the diamides (Figure 2). Within the limits of this assumption, in some cases it is even possible to assign signals given by a specific amide group (*E* or *Z*) in different diastereomeric sequences. The assignments are reported in Figure 3 and in the Tables II and III. As shown, the amide groups of the polyamides behave qualitatively like the corresponding groups of the model compounds, the -ac- groups having predominantly, if not exclusively, the *E*-configuration and the -bc- groups the *E*-configuration or, preferably, the *Z*-configuration. In comparison with the amide groups of the models, there are, however, significant quantitative differences. Thus, the -bc- groups of PI and PII are distributed in the two configurations with a [*Z*]/[*E*] ratio (Table I), which is higher than that found for the -bc- groups of MIII and MII, respectively (Table IV). Furthermore, the -bc- groups of PIII in ODCB-d_4 give a [*Z*]/[*E*] ratio (1.56;

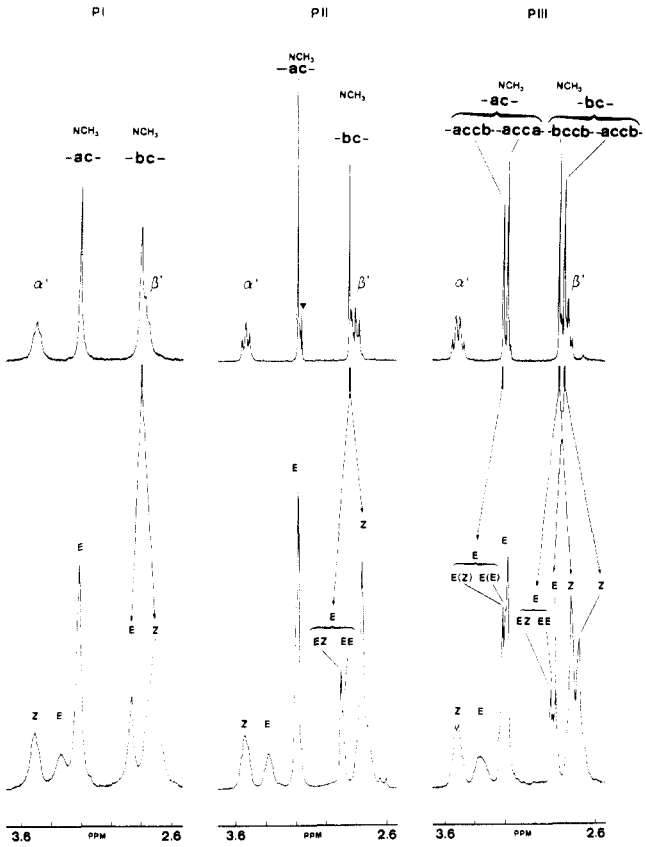


Figure 3. Partial ^1H NMR spectra of the polyamides in ODCB-d_4 showing the region of the NCH_3, $CH_2(\alpha')$, and $CH_2(\beta')$ signals: top, 120 °C; bottom, 25 °C. The arrows indicate the splitting of the NCH_3 signals, which takes place on lowering the solution temperature. The black triangle in the 120 °C spectrum of PII indicates an impurity.

Table IV
Constants of the Configurational Equilibrium for the Diamides, [Z]/[E] Ratios for the -bc- Groups, and Activation Energies, ΔG^*, for the $Z \rightarrow E$ Isomerization of These Groups (T, 25 °C; ODCB-d_4)

		equilibrium constants[a]			
amide	solvent	$\frac{[ZZ]^b}{[EZ]}$	$\frac{[EZ]^b}{[EE]}$	$\frac{[Z]^b}{[E]}$	ΔG^{*c}
MI	ODCB-d_4	<0.05	<0.05		
	$CDCl_3$	<0.05	0.22		
MII	ODCB-d_4	0.74	2.61	1.41	17.7[d]; 17.7[e]
	$CDCl_3$	0.68	2.24	1.25	*g*
	$CDCl_3/C_6D_6$[f]	0.56	2.27	1.13	*g*
	DMSO-d_6	0.53	1.68	0.94	*g*
MIII	ODCB-d_4	<0.05[h]	1.33[h]	1.33	18.0[e]
	$CDCl_3$	0.06[h]	1.16[h]	1.16	*g*

[a] [*EE*], [*EZ*], and [*ZZ*] are the molar concentrations of the different diastereomeric species. [b] Estimated error ±2%. [c] Kilocalories per mole degree. [d] $ZZ \rightarrow EZ$. [e] $EZ \rightarrow EE$. [f] 42% C_6D_6 by volume. [g] Not determined. [h] The *E*-configuration in the *EZ*-isomer is that of the -ac- groups.

Table I) higher than would be expected (1.37) if the groups would behave as those of the model compounds. We suggest that this higher proportion of -bc- groups in the *Z*-configuration may serve to relax steric interactions that in the polyamides can be more restrictive than in the low molecular weight models. The values of the [*Z*]/[*E*] ratio found for the -bc- groups of the three isomeric polyamides are not significantly different. Since the results obtained with the model diamides (see above) leave little doubt that the different constitution of these polyamides must determine differences in their configurational characteristics, the differences in the [*Z*]/[*E*] ratio must lie within the limits set by the estimated precision of the analytical method used, namely between 0.10 and 0.17.

Conclusions

Although this work has failed to reveal large differences in the physical properties of the N-methylated, isomeric polyamides investigated, it has produced some interesting results on their configuration in solution. In particular, the NMR analysis (i) has shown that there are significant differences in the preferences of the amide groups between the polymers and low molecular weight models and (ii) has provided indirect evidence that the configurational characteristics of the polymers are influenced by their constitution.

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References and Notes

(1) Pino, P.; Lorenzi, G. P.; Suter, U. W.; Casartelli, P. G.; Steinmann, A.; Bonner, F. J.; Quiroga, J. A. *Macromolecules* **1978**, *11*, 624.
(2) Schmucki, M. A.; Pino, P.; Suter, U. W. *Macromolecules* **1985**, *18*, 823.
(3) Deschenaux, R.; Neuenschwander, P.; Pino, P. *Helv. Chim. Acta* **1986**, *69*, 1349.
(4) Meyer, W. R.; Gentile, F. T.; Suter, U. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28* (2), 290.
(5) Bovey, F. A.; Ryan, J. J.; Hood, F. P. *Macromolecules* **1968**, *1*, 305.
(6) Miron, Y.; McGarvey, B. R.; Morawetz, H. *Macromolecules* **1969**, *2*, 154.
(7) Shalaby, S. W.; Fredericks, R. J.; Pearce, E. M.; Wenner, W. M. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 223.
(8) Tsvetkov, V. N.; Koton, M. M.; Shtennikova, I. N.; Laurenko, P. N.; Peker, T. V.; Okatova, O. V.; Novakowskii, V. B.; Nosova, G. I. *Vysokomol. Soedin. Ser. A* **1979**, *21*, 1711.
(9) Johnstone, R. A. W.; Payling, D. W.; Thomas, C. *J. Chem. Soc. C* **1969**, 2223.
(10) Pailer, M.; Hübsch, W. J. *Monatsh. Chem.* **1966**, *97*, 1541.
(11) Hill, J. W. *J. Am. Chem. Soc.* **1930**, *52*, 4110.
(12) Vogt, H.; Rosenberg, W. *Arch. Pharm.* **1954**, *287*, 514.
(13) Moroder, L.; Hallett, A.; Wünsch, E.; Keller, O.; Wersin, G. *Hoppe-Seyler's Z. Physiol. Chem.* **1976**, *357*, 1651.
(14) Olsen, R. K. *J. Org. Chem.* **1970**, *35*, 1912.
(15) Lynden-Bell, R. *Prog. NMR Spectrosc.* **1967**, *2*, 163.
(16) Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961.
(17) Wu, G. C.; Tanaka, H.; Sanui, K.; Ogata, N. *Polym. J.* **1982**, *14*, 571.
(18) Wu, G. C.; Tanaka, H.; Sanui, K.; Ogata, N. *Polym. J.* **1982**, *14*, 797.
(19) Suter, U. W.; Pino, P. *Macromolecules* **1984**, *17*, 2248.
(20) Giesekus, H. In *Polymer Fractionation*; Cantow, M. J. R., Ed.; Academic Press: New York, 1967; p 191.
(21) Lee, L. T. C. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2025.
(22) Hatton, J. V.; Richards, R. E. *Mol. Phys.* **1960**, *3*, 253.
(23) Hatton, J. V.; Richards, R. E. *Mol. Phys.* **1962**, *5*, 139.
(24) LaPlanche, L. A.; Rogers, M. T. *J. Am. Chem. Soc.* **1963**, *85*, 3728.
(25) Xie, G.; Gramlich, V.; Lorenzi, G. P., to be published.
(26) Pedersen, B. F.; Pedersen, B. *Tetrahedron Lett.* **1965**, *34*, 2995.
(27) Carter, R. E. *Acta Chem. Scand.* **1967**, *21*, 75.