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### <sup>13</sup>C-NMR Sequence Analysis. 23. Synthesis and NMR Spectroscopic Characterization of Polyoxamides with Alternating and Random Sequences of Aliphatic Diamines

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## **<sup>13</sup>C-NMR Sequence Analysis. 23. Synthesis and NMR Spectroscopic Characterization of Polyoxamides with Alternating and Random Sequences of Aliphatic Diamines**

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### ABSTRACT

Three classes of polyoxamides were prepared: homopolymers derived from  $\alpha$ -,  $\omega$ -diaminoalkanes, and 4,4'-diaminodiphenylmethane, copolymers with an alternating sequence of two different aliphatic diamines and copolymers with a random sequence of two different diamines. For their syntheses a new class of monomers, the diamine bisoxamide diethyl esters, were prepared from  $\alpha,\omega$ -diamines and oxalic acid chloride ethyl ester. The 22.63 MHz <sup>13</sup>C-NMR spectra of the polyoxamide solution in fluoro-sulfonic acid permitted sequence analysis because the carbonyl signals are sensitive to the nature of the neighboring diamine units. In contrast, 9.12 MHz <sup>15</sup>N-NMR spectra did not give any sequence information. The thermal stability of the polyoxamides was investigated, but differential scanning calorimetry did not give useful information on the crystallinity of the polyoxamides because of their thermal degradation.

## INTRODUCTION

Poly(oxamide)s are an interesting class of polyamides because the high concentration of H-bonds gives good mechanical properties and because copoly(oxamide)s have useful properties as membranes for reverse osmosis [1]. Unfortunately, investigations of poly(oxamide)s suffer from the fact that they are difficult to synthesize. In contrast to the syntheses of other aliphatic polyamides, the thermal condensation of oxalic acid with diamines is not successful owing to the decarboxylation of oxalic acid. The high sensitivity of oxalyl chloride to hydrolysis prevents its application under the usual conditions of interfacial polycondensations [3]. This problem was partially solved by Sokolov [3-5] who introduced gaseous oxalyl chloride diluted with nitrogen into warm alkaline solutions of aliphatic diamines. However, this procedure is relatively complicated, and it is not suited for syntheses of nylon-2,2 or poly(oxamide)s with an alternating sequence of two diamines. Furthermore, the ring-opening polymerization of cyclic oxamides is limited to the synthesis of a few homopolymers [6] and the condensation of the s.c. diamine oxamides [7-9] is designed for the preparation of copolyamides built up by two or more different diacids. The purpose of the present work was threefold. Since dimethyl and diethyl oxalate are relatively cheap, technically available starting materials and because alkyl oxalates are more electrophilic than esters of other diacids, their usefulness in condensation reactions should be investigated. Furthermore, a procedure for the preparation of poly(oxamide)s with an alternating sequence of two (or more) different diamines should be found. Finally, the  $^{13}\text{C}$ - and  $^{15}\text{N}$ -NMR spectra of copoly(oxamide)s with regular and random sequences of different diamine units should be studied, to complete our sequence analysis of copolyamides and copolyureas [10-16].

## EXPERIMENTAL

Measurements

The IR spectra were recorded on a Unicam SP 1000 spectrophotometer. KBr disks were prepared from 2 mg of a product and 200-250 mg KBr.

The melting points were determined on a hot stage apparatus and are not corrected.

The viscosities were measured in a 0.4 mm i.d. Ostwaldt viscosimeter at  $25 \pm 0.1^\circ\text{C}$  using 0.5 w/v% solutions of polyamides in conc sulfuric acid.

The thermogravimetric analyses were conducted with a Perkin-Elmer TGS-2 thermobalance at a heating rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere.

The 22.63 MHz  $^{13}\text{C}$ -NMR spectra were obtained on a Bruker WH-90 FT spectrometer at 28–30°C. Solutions of 300 mg polyamide in 1.8 mL fluorosulfonic acid (FSA) were measured in 10 mm o.d. sample tubes with a coaxial 4 mm o.d. tube containing a 1:1 mixture (by volume) of dioxane- $d_8$  and TMS for shift referencing and lock purposes. The following acquisition parameters were used: pulse width 8  $\mu\text{s}$  ( $\sim 70^\circ$ ), 8 K data points/5000 Hz spectral width zero filled to 16 K before Fourier-transform, exponential line-broadening 0.8 Hz, and  $\sim 4,000$  transients for homopolymers and 10,000 transients for copolymers.

The 9.21 MHz  $^{15}\text{N}$ -NMR measurements were also conducted on a Bruker WH-90 FT spectrometer, and 20 mm o.d. sample tubes with a 5-mm o.d. coaxial tube containing a 25% (by weight) solution of  $^{15}\text{NH}_4^+$   $^{15}\text{NO}_3^-$  in  $\text{D}_2\text{O}$  were used. The acquisition parameters were: pulse width 60  $\mu\text{s}$  ( $\sim 70^\circ$ ), 1 K data points/500 Hz spectra width zero filled to 2 K before Fourier-transform, and exponential line-broadening 1 Hz 4,000–16,000 transients.

## Materials

The solvents and triethylamine were dried and purified by distillation over  $\text{P}_4\text{O}_{10}$ , calcium hydride, or sodium wire, depending on their chemical stability. The aliphatic diamines were distilled in vacuo over freshly powdered calcium hydride. Diethyl oxalate was used as purchased from EGA Chemie (D. Steinheim, West Germany). The acid chloride of ethyl oxalate was prepared from the potassium salt of ethyl oxalate and thionyl chloride according to Ref. 17.

## Monomers

The following two procedures are given as examples for the preparation of the monomers listed in Table 1.

A) 4,4'-Diaminodiphenyl methane bisoxamide diethyl ester: 21.84 g (0.16 mol) of oxalyl chloride ethyl ester was added under stirring to a cooled solution of 15.84 g (0.08 mol) of 4,4'-diaminodiphenylmethane and 16.16 g (0.16 mol) of triethylamine in 100 mL of dry N,N-dimethylformamide. After 1 h at 0°C a copious white precipitate was formed. The reaction mixture was stirred for an additional hour at room temperature and then poured into 500 mL of distilled water. The washed and dried crude product (yield: 94%) was recrystallized twice from ethanol; mp 149°C.

B) 1,2-Diaminoethane bisoxamide diethyl ester: 108.6 g (2 mol) of trimethylchlorosilane was added dropwise under stirring to a cooled solution of 60.1 g (1 mol) of ethylenediamine and 202.5 g (2 mol) of triethylamine in 1000 mL of dry methylene chloride. The mixture was

TABLE 1. Properties of Various Diamine Bisoxamide Diethyl Esters with the Formula  
 $\text{CH}_3\text{-CH}_2\text{-O-CO-CO-NH-A-NH-CO-CO-O-CH}_2\text{-CH}_3$

A	mp ( $^{\circ}\text{C}$ )	Elementary formula (mol wt)	Elemental analyses		
			C	H	N
$\text{-(CH}_2\text{)}_2\text{-}$	129-130	$\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_6$ (260.25)	Calc 46.15 Found 45.96	6.15 6.14	10.77 11.00
	89-90	$\text{C}_{11}\text{H}_{18}\text{N}_2\text{O}_6$ (274.28)	Calc 48.16 Found 48.32	6.61 6.47	10.22 10.00
$\text{-(CH}_2\text{)}_3\text{-}$	108-109	$\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_6$ (288.31)	Calc 50.01 Found 50.14	6.84 6.87	9.72 9.87
	88-89	$\text{C}_{14}\text{H}_{24}\text{N}_2\text{O}_6$ (316.36)	Calc 53.18 Found 53.38	7.59 7.87	8.85 9.36
$\text{-(CH}_2\text{)}_4\text{-}$	148-150	$\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_6$ (398.45)	Calc 63.31 Found 63.37	5.58 5.67	7.03 7.22

refluxed for 3 h. On cooling, 250 mL of ligroin was added, and the mixture was cooled to  $0^\circ\text{C}$  to complete the precipitation of triethylamine hydrochloride, which was finally filtered off under exclusion of moisture. After evaporation of the solvent the  $N,N'$ -bistrimethylsilyl diamino ethane was distilled at  $111\text{--}114^\circ\text{C}/14$  mbar, yield: 74%.

0.5 mole of  $N,N'$ -bistrimethylsilylethyldiamine was reacted with 1 mol of oxalyl chloride ethyl ester in 500 mL of dry ethyl acetate for 5 h at room temperature. The crystals of dioxamide formed during the reaction were filtered off, the filtrate was concentrated to dryness and the remaining white solid was combined with the first batch of product. The crude reaction product was treated twice with charcoal in boiling ethanol and recrystallized from ethanol; yield: 78%.

### Polycondensations

All polycondensations were conducted in dry *m*-cresol because attempts to use nonprotic solvents, such as dimethylformamide or diphenylsulfone, resulted in lower viscosities of the resulting polymers.

A) Condensations of diethyl oxalate: In a typical experiment 1.50 g (25 mmol) of 1,2-diaminoethane and 5.01 g (25 mmol) of 1,12-diaminododecane were heated with 7.3 g (50 mmol) of dimethyl oxalate in 120 mL of dry *m*-cresol to  $180^\circ\text{C}$ . The reaction mixture was stirred at this temperature under nitrogen for 5 h. After  $\sim 2$  h the distillation of ethanol had ceased. The viscous reaction mixture was poured into 2 L of acetone, the precipitated polyoxamide was isolated by filtration and washed several times with acetone. The crude yellowish polymer was extracted with tetrahydrofuran for 10 h in a Soxhlet-apparatus and dried at  $70^\circ\text{C}/12$  mbar, yield 85%. Analysis: Calculated for  $\text{C}_{18}\text{H}_{32}\text{N}_4\text{O}_4$  (368.49): C, 58.67; H, 8.75; N, 15.21. Found: C, 60.69; H, 9.19; N, 14.17.

B) Condensation of 1,2-diaminoethane bisoxamide diethyl ester: In a typical experiment 13.01 g (50 mmol) of the bisoxamide diethyl ester IVa and 10.02 g (50 mmol) 1,12-diaminododecane were heated in 120 mL of dry *m*-cresol to  $180^\circ\text{C}$ . The reaction mixture was stirred at this temperature for 4 h under a slow stream of nitrogen, whereby the theoretical amount of ethanol was collected. Then the viscous reaction mixture was worked up as described for Method A; yield: 88%. Analysis: Calculated for  $\text{C}_{18}\text{H}_{32}\text{N}_4\text{O}_4$  (368.49): C, 58.67; H, 8.75; N, 15.21. Found: C, 58.75; H, 8.88; N, 15.36.

## RESULTS AND DISCUSSION

Since the most reactive and least expensive ester of oxalic acid is the diethyl ester, this monomer was used for the preparation of homopolyamides and copolyamides with random sequences of different di-

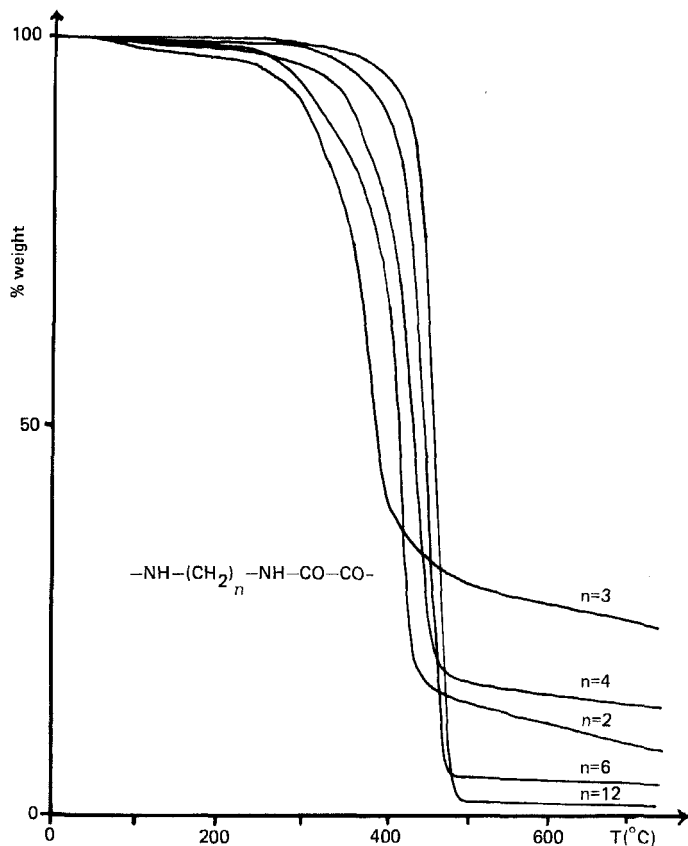
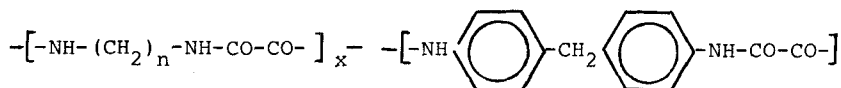


FIG. 1. Thermogravimetric analyses of the polyoxamides Ia-e measured at a heating rate of  $10^\circ\text{C}/\text{min}$  in nitrogen.

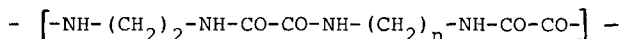
amines. Although the ester groups prevent thermal decarboxylation, bulk condensations of oxalic acid diethyl ester and diamines in the melt are not successful. The main reasons for the failure of bulk condensations are the relatively low thermostability of poly(oxamide)s and the high melting points ( $>300^\circ\text{C}$ ) of aromatic poly(oxamide)s and aliphatic poly(oxamide)s with short alkylene chains. The low thermostabilities of our homopolyamides Ia-e are demonstrated in Fig. 1. The degradation of all poly(oxamide)s begins below  $300^\circ\text{C}$  and in the case of nylon-2,2 and nylon-3,2 (Ib) the thermal decomposition sets in even below  $200^\circ\text{C}$ . The greatest thermostability is found for the poly(oxamide) of 1,12-diaminododecane (Ie) followed by that of the 1,6-hexamethylene diamine polymer (Id). This order corresponds

roughly to that of the molecular weights. In the case of other aliphatic polymers the thermostability decreases with increasing length of the aliphatic chain because the methylene groups are sensitive to oxidation. Hence, we suppose that the low thermostability of Ia and Ib is partially a result of the low molecular weights, because the formation of cyclic oxamides via a zip-mechanism is favored by a high concentration of chain ends.



I a - e

II



III a - e

a: n = 2

d: n = 6

b: n = 3

e: n = 12

c: n = 4

The condensation of diethyl oxalate and diamines in a liquid reaction medium at temperatures below  $200^\circ\text{C}$  requires a good solubility of the resulting oligo- or poly(oxamide)s in this medium. However, solvents such as dichloro- or trifluoroacetic acid are too acidic and protonate the diamines. In aprotic solvents, such as dimethylformamide and diphenyl sulfone, the precipitation of oligomers prevented the formation of polymers. Thus, *m*-cresol seemed to be the best compromise and was used for all condensations (Table 2). Also, in this solvent poor results were obtained when diethyl oxalate was reacted with 1,2-diaminoethane, 1,3-diaminopropane, or 1,4-diaminobutane. In the case of 1,2-diaminoethane we were able to isolate the cyclic monomer 2,3-dioxopiperazine which indicates that, as expected, cyclization is the most frequent side reaction when short alkylene diamines are used as monomers. In agreement with this interpretation we found high yields and relatively high viscosities when 1,6-diaminohexane or 1,12-diaminododecane were condensed (Nos. 4 and 5; Table 2). Vogl et al. [1] reported an inherent viscosity of 0.64 dL/g for nylon-6,2 prepared by an improved "Sokolov procedure." Thus, the molecular weights of our nylon-6,2 and nylon-12,2 samples compete well or even outstrip the highest values reported in the literature.



TABLE 2. Reaction Conditions and Results of Syntheses of Various Poly(oxamide)s from  $\alpha,\omega$ -Diamino Alkanes or 4,4'-Diaminodiphenylmethane in *m*-Cresol

No.	Diamines	Method <sup>a</sup>	Temperature (°C)	Time (h)	Yield <sup>b</sup> (%)	$\eta_{inh}^c$ (dL/g)	Nitrogen, calc	Analyses, found
1	1,2-Diaminoethane	B	170	8	55	0.13	24.56	24.85
2	1,3-Diaminopropane	B	170	8	54	0.15	21.88	22.30
3	1,4-Diaminobutane	B	170	6	85	0.26	19.71	19.50
4	1,6-Diaminohexane	B	180	5	95	0.66	16.46	16.86
5	1,6-Diaminohexane	A	180	5	93	0.61	16.46	16.61
6	1,12-Diaminododecane	A	180	5	99	1.00	11.02	11.36
7	4,4'-Diaminodiphenylmethane	A	200	6	60	-	-	-
8	1,2-Diaminoethane 1,3-Diaminopropane	} alternating B	180	4	60	0.15	23.12	23.13
9	1,2-Diaminoethane 1,4-Diaminobutane	} alternating B	180	4	65	0.19	21.86	20.97
10	1,2-Diaminoethane 1,6-Diaminohexane	} alternating B	180	4	90	0.23	19.71	18.86
11	1,2-Diaminoethane 1,12-Diaminododecane	} alternating B	180	4	88	0.35	15.21	15.36

12	1,2-Diaminoethane 4,4'-Diaminodiphenyl- methane	}alternating	B	180	6	65	-	-	-
13	1,2-Diaminoethane 1,3-Diaminopropane	}random	A	170	6	5	0.13	23.13	22.98
14	1,2-Diaminoethane 1,4-Diaminobutane	}random	A	170	6	65	0.13	21.86	20.66
15	1,2-Diaminoethane 1,6-Diaminohexane	}random	A	170	5	80	0.21	19.71	18.88
16	1,2-Diaminoethane 1,12-Diaminododecane	}random	A	170	4	85	0.24	15.21	14.17
17	1,2-Diaminoethane 4,4'-Diaminodiphenyl- methane	}random	A	180	6	61	-	-	-
18	1,6-Diaminohexane 1,12-Diaminododecane	}random	A	170	6	93	0.88	13.74	13.65

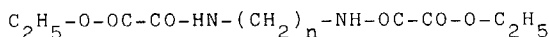
<sup>a</sup>A: diethyl oxalate + diamines, B: diamine bisoxamide diethyl ester diamines.

<sup>b</sup>After precipitation from methanol.

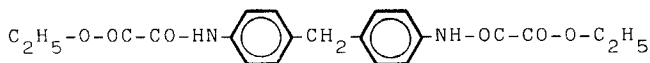
<sup>c</sup>Measured with  $c = 5$  g/L in conc sulfuric acid.

When random copoly(oxamide)s were prepared from diethyl oxalate and equimolar mixtures of two different diamines (Nos. 13-18, Table 2), the results correspond well to those obtained for the homopolymers. With 1,2-diaminoethane as reaction partner, which was preferred for spectroscopic reasons (see below), both yield and viscosities were relatively low. Furthermore, the elemental analyses (Table 2 and experimental part) and the  $^{13}\text{C}$ -NMR spectra indicate that 1,2-diaminoethane is to a lesser extent incorporated than all higher diaminoalkanes. Obviously the formation of cyclic by-products is responsible for these results. When a mixture of 1,6-diaminohexane and 1,12-diaminododecane is used, both yield and viscosity were satisfactory (No. 18, Table 2) and compare well with the data of the corresponding homopolymers Id-e.

Nonetheless, the condensation of diethyl oxalate (Method A) did not enable us to synthesize nylon-2,2, and both yields and viscosities of nylon-3,2 and nylon-4,2 were below those values given for Method B in Table 2. Furthermore, Method A is principally not suited for the synthesis of alternating sequences (IIIb-e). Therefore, a new class of monomers was synthesized, the so-called diamine bisoxamide diethyl esters IVa-d and V. In the case of aromatic diamines these monomers are easily attainable by acylation of the diamines with oxalyl chloride monoethyl ester in the presence of triethylamine. However, this method failed when aliphatic diamines were to be acylated, because the precipitation of diamine hydrochlorides competes with their acylation.



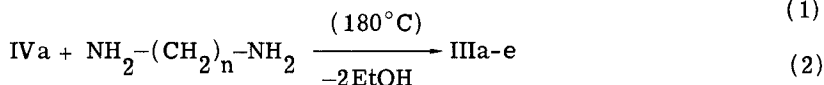
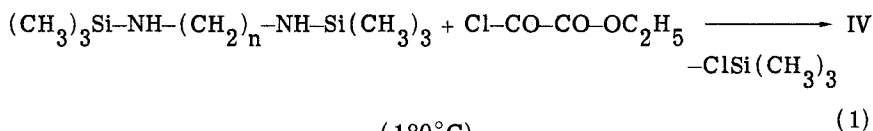
IVa-d



V

Satisfactory results were obtained when the N,N'-bistrimethylsilyl diaminoalkanes were acylated (Eq. 1 and Table 1). The bisoxamide esters IVa-d were condensed with various diamines in m-cresol (Method B, Table 2). This method prevents the formation of large amounts of cyclization products and gave moderate yields of nylon-2,2 and nylon-3,2. The successful syntheses of the alternating copolyoxamides IIIb-e, furthermore, demonstrates that this reaction pathway does not involve transamidation. A short-coming of this

method is that only low molecular weights (viscosities, Table 2) were obtained for the resulting sequence polyamides, yet for our spectroscopic investigations they were sufficiently high.



### $^{13}\text{C}$ - and $^{15}\text{N}$ -NMR Spectroscopy

In previous papers we have described  $^{13}\text{C}$ - and  $^{15}\text{N}$ -NMR sequence analyses of various copolyamides [10-15] and copolyureas [16]. The copolyamides were built up either by two or more  $\omega$ -amino acids or by two (or more) diamines and diacids. As discussed recently,  $^{13}\text{C}$ -NMR sequence analysis is superior to  $^{15}\text{N}$ -NMR sequence analysis in most cases of copolyamides [15]. The  $^{13}\text{C}$ -NMR spectra of the binary copolyamides exhibit four carbonyl signals representing the four different types of amide groups that can occur in such a copolyamide. The average lengths of the homogeneous blocks may then be calculated from the intensity ratios of the CO signals. Correspondingly, ternary copolyamides can show up to nine different CO signals [13] which allow the characterization of the sequence. Also the CO signals of the  $^{13}\text{C}$ -NMR spectra of copolyureas are sensitive to the nature of both neighboring diamine units, and thus, can be used for the purpose of sequence analyses. However, the  $^{13}\text{C}$ -NMR carbonyl signals partially overlap with solvent signals, whereas the  $^{15}\text{N}$ -NMR signals are more sensitive to sequence effects and are never obscured by solvent signals. In contrast to all copolyamides studied previously, polyamides built up by one diacid and two (or more) diamines or by one diamine and two (or more) diacids were never analyzed by means of  $^{13}\text{C}$ - or  $^{15}\text{N}$ -NMR spectroscopy. Such copolyamides possess two different kinds of amide groups and sequence effects in their NMR spectra are only expected if far-reaching "neighboring residues" exist. In the case of alternating copolyamides composed of ethylenediamine and two different diacids, the  $^1\text{H}$ -NMR signals of the ethylenediamine units were found [19] to be sensitive to the nature of the neighboring diacids, and thus, allowed the authors to characterize the sequence.

In the case of copolyamides built up by one diacid and two different diamines we have investigated copolymers prepared from succinyl chloride or adipoylchloride, on the one hand, and equimolar mixtures of 1,6-diaminohexane and 1,12-diaminododecane on the other hand. In these cases neither 270 MHz  $^1\text{H}$ -NMR nor 22.63 MHz  $^{13}\text{C}$ -NMR nor 9.12 MHz  $^{15}\text{N}$ -NMR spectra gave any sequence information. Only two

carbonyl signals, two nitrogen signals, and two N-CH<sub>2</sub> proton signals representing the two different kinds of amide groups were detectable. Poly(oxamide)s, which have an intermediate structure between of polyureas and polyamides, were more promising with respect to <sup>13</sup>C. Due to the better solubility and due to a better resolution of the CO signals, the <sup>13</sup>C-NMR spectra of all poly(oxamide)s were measured in fluoro-sulfonic acid and not in trifluoroacetic acid which is a good NMR solvent for polyureas [16] and polyurethanes [20]. The chemical shifts of the homopolymers listed in Table 3 show that the CO signals absorb at higher field (lower frequency) with increasing chain length of the diamine unit. A similar chemical shift/chain length relationship was found for the <sup>13</sup>C-NMR spectra of polyureas [16]. However, the chemical shift/chain length relationship of all polyamides we have investigated so far has exactly the opposite sense [10-12]. Increasing down-field shift with increasing chain length of the monomer units is easily understandable, because aliphatic substituents enhance the basicity of amide groups, the degree of protonation and thus the anisotropy. However, we are currently not able to explain the inversion of the substituent effects. In this connection, it is noteworthy to mention that also in the case of polyoxamides a monotonic chemical shift/chain length curve is found, which means that irregularities, such as the s.c. "γ-effect," are absent.

From the viewpoint of sequence analysis, the most interesting result is that the CO signals of the alternating copolyoxamides differ by more than 1 ppm from those of the homopolymers. Furthermore, two carbonyls are observable and their shift difference increases with increasing difference of the chain length of the diamine units (i.e., in the order IIIa-IIIe). Correspondingly, the <sup>13</sup>C-NMR spectra of the random copolymers display four CO signals. Two of them have chemical shifts which agree with those of the homopolymers, and thus were attributed to the homogeneous blocks (A-A or B-B bonds) (Fig. 2C). The inner pair of CO signals agrees with those of the alternating copolymers and thus must originate from the cross-over steps (A-B and B-A bonds) (Fig. 2B). Since for kinetic reasons the cross-over steps must have identical frequencies, their signal intensities must be equal. The average lengths of the homogeneous blocks  $\bar{L}_A$  and  $\bar{L}_B$  are then easily calculated from the signal intensities:

$$\bar{L}_A = \frac{\bar{I}_{AA}}{\bar{I}_{AB}} + 1 \quad \text{and} \quad \bar{L}_B = \frac{\bar{I}_{BB}}{\bar{I}_{BA}} + 1$$

In this way we found that all three "random copolyoxamides" (Nos. 14-16, Table 2) possess an  $\bar{L}_A = 3.0 \pm 0.2$  for the blocks made up of

TABLE 3.  $^{13}\text{C}$ -NMR Chemical Shifts  $\delta$  (ppm, relative to external TMS) of Aliphatic Polyoxamides Measured in Fluorosulfonic Acid

Diamine units	$\delta$					
	CO	$\alpha$ -C	$\beta$ -C	$\gamma$ -C	$\delta$ -C	$\epsilon$ -C
1,2-Diaminoethane	160.20	46.36	-	-	-	
1,3-Diaminopropane	159.07	42.45	28.51	-	-	
1,4-Diaminobutane	157.62	41.00	24.65	-	-	
1,6-Diaminohexane	157.02	40.94	26.05	27.35	-	
1,2-Diaminododecane	156.70	40.88	26.65	27.67	29.02	29.40
1,2-Diaminoethane +	158.91	45.09	-	-	-	-
1,4-Diaminobutane (alternating)	158.80	40.94	24.65	-	-	-
1,2-Diaminoethane +	158.97	46.33	-	-	-	-
1,6-Diaminohexane (alternating)	158.26	40.83	26.10	27.40	-	-
1,2-Diaminoethane +	159.24	46.98	-	-	-	-
1,12-Diaminododecane (alternating)	158.32	41.10	26.92	27.94	29.34	29.66
1,2-Diaminoethane +	160.32 159.00	45.05	-	-	-	-
1,4-Diaminobutane (random)	158.83 157.60	41.01	24.67	-	-	-
1,2-Diaminoethane +	160.30 158.97	46.87 46.27				-
1,6-Diaminohexane (random)	158.26 156.97	40.94	26.10	27.40	-	-
1,2-Diaminoethane +	160.35 159.27	46.95				
1,12-Diaminododecane (random)	158.29 156.67	40.90	26.68	27.70	29.00	29.38

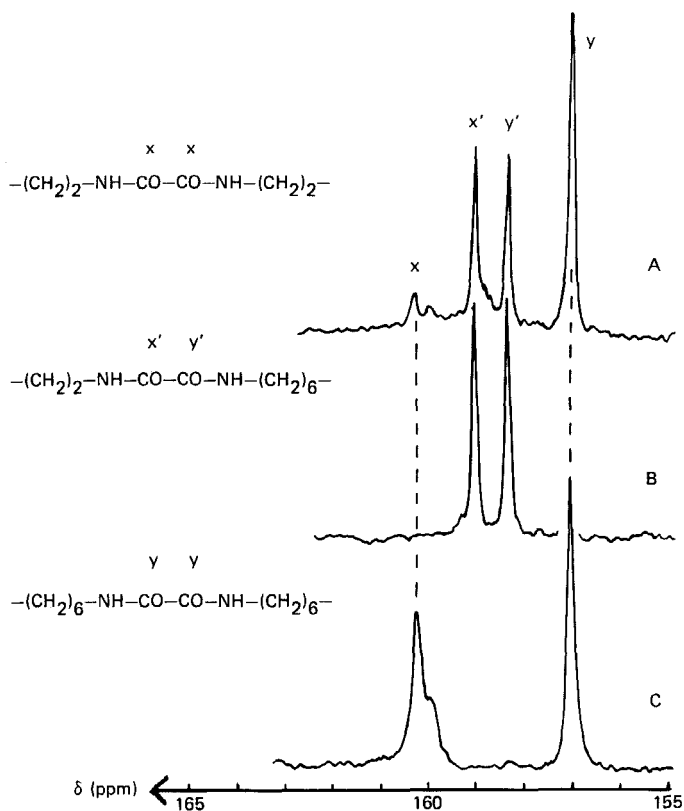


FIG. 2. Carbonyl signals in the 22.63 MHz  $^{13}\text{C}$ -NMR spectra of polyoxamides measured in fluorosulfonic acid: (A) random copolymer No. 15, Table 2; (B) alternating copolymer No. 10, Table 2; (C) mixture of homopolymers Ia and Ie.

long diamine units (signal y in Fig. 2A) and an  $\bar{L}_B = 1.2 \pm 0.1$  for the blocks of 1,2-diaminoethane sequences (signal x in Fig. 2A). Furthermore, it turned out that the CO signals of nylon-2,2 and of the nylon-2,2 blocks of the random copolymers are broader than the other CO signals and exhibit a shoulder  $\sim 0.3$  ppm at higher field (Figs. 2A and 2C). We suppose that contamination with cyclic oligoamides and end-group effects are responsible for this observation, inasmuch as our nylon-2,2 possessed the lowest viscosity value of all poly(oxamide)s (No. 1, Table 2).

Finally, we have measured the  $^{15}\text{N}$ -NMR chemical shifts of the homopolymers Ia-e and of the alternating sequences IIIb-e (Table 4).

TABLE 4.  $^{15}\text{N}$ -NMR Chemical Shifts  $\delta$  (ppm) Upfield of External  $\text{NO}_3^-$  of Polyoxamides in Trifluoroacetic Acid

Polyoxamide of	$\delta$	Alternating copolyoxamide of	$\delta$
1,2-Diaminoethane	-261.3	1,2-Diaminoethane +	-261.2
1,3-Diaminopropane	-257.3	1,3-Diaminopropane	
1,4-Diaminobutane	-255.3	1,2-Diaminoethane +	-261.2
1,6-Diaminohexane	-253.9	1,4-Diaminobutane	
1,10-Diaminododecane	-253.0	1,2-Diaminoethane +	-261.2
		1,6-Diaminohexane	-253.8
		1,2-Diaminoethane +	-261.1
		1,12-Diaminododecane	-252.9

For these measurements trifluoroacetic acid was the preferred solvent because it is less viscous and yields a favorable nuclear Overhauser effect [19]. As expected, the spectra of the alternating copolymers displayed two signals, yet their chemical shifts were identical with those of the corresponding homopolymers. Hence, in sharp contrast to polyureas, polyoxamides are not suited for  $^{15}\text{N}$ -NMR sequence analyses. This result is noteworthy because sequence effects of several ppm were found in the  $^{15}\text{N}$ -NMR spectra of polyureas and because long-range neighboring residue effects (ranging over distances of several  $\alpha$ -bonds) were observed in the spectra of various copolyamides [15]. Obviously, both the  $^{13}\text{C}$ - and the  $^{15}\text{N}$ -NMR spectra of polyoxamide show unusual properties. However, it is noteworthy that the chemical shift/chain length relationship of the  $^{15}\text{N}$ -NMR measurements shows the usual behavior, i.e., increasing chain length results in downfield shifts in close analogy with other polyamides [10] and polyureas [16].

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