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^{15}N-NMR Spectroscopy. XVIII. Sequence Analysis of Linear Polyureas

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^{15}N-NMR Spectroscopy. XVIII. Sequence Analysis of Linear Polyureas*

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ABSTRACT

Various homo- and copolyureas were prepared either by conversion of diamines with diisocyanates or by heating diamines with N,N'-bisphenoxycarbonyl diamines. The ^{13}C-NMR spectra and the natural abundance ^{15}N-NMR spectra were measured in trifluoroacetic acid. In contrast to polyamides, the carbonyl signals of polyureas are not sensitive to neighboring residue effects, so that ^{13}C-NMR spectra are in most cases useless for the sequence analysis of copolyureas. The ^{15}N-NMR signals of urea groups are, however, sensitive to the influence of both substituents and thus contain information on the sequence. Structure/shift-relationships are discussed, and ^{15}N-NMR spectra of various copolyureas are presented.

INTRODUCTION

In previous papers we have discussed the usefulness of ^{13}C- and ^{15}N-NMR spectroscopy for the characterization of copolyesters [1],

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*For Part XVII see H. R. Kricheldorf and W. E. Hull, Makromol. Chem., 180, 1715 (1979).

copolyamides [2-7], and polypeptides [8-12]. It was our intention in this work to extend these studies on polyureas. Polyureas are industrially produced, and urea groups are also formed in the course of the synthesis of polyurethanes. Thus, a sensitive and routine analytical method is desirable for the characterization of polyureas, inasmuch as IR and ^{1}H-NMR spectroscopy do not allow to identify individual urea groups in copolymers of various structure.

EXPERIMENTAL

Materials

The diisocyanates were distilled before use. The aliphatic diamines were recrystallized by using charcoal decolorization. Dimethylformamide and dimethylacetamide were dried by distillation over P_4O_{10} in vacuo.

N,N'-Bisphenoxycarbonyl-1.2-diaminoethane

A mixture of 18 g (0.3 mole) 1,2-diaminoethane and 85 ml (0.6 mole) triethylamine dissolved in 200 ml methylene chloride was added dropwise under cooling with ice to a solution of 95 g ($>$ 0.6 mole) phenol chloroformate in 400 ml methylene chloride. Afterwards the reaction mixture was diluted with 200 ml methylene chloride and 200 ml tetrahydrofuran and washed twice with 300-ml portions of 1 N hydrochloric acid. The organic phase was dried over sodium sulfate. After the solution was concentrated in vacuo, the product was crystallized by addition of carbon tetrachloride under cooling with ice. Yield, 81%; mp, 199-201°C.

ANAL. Calcd. for $C_{16}H_{16}N_2O_4$: C 63.98%; H 5.37%; N 9.23%. Found: C 63.56%; H 5.58%; N 9.23%.

Polyethyleneurea

N,N'-Bisphenoxycarbonyldiaminoethane (30 g, 0.1 mole) and 6.0 g (0.1 mole) 1,2-diaminoethane were heated under stirring in ml dry N,N'-dimethylacetamide to 140°C for 8 hr. Afterwards the reaction mixture was poured into a beaker with 1 liter hot ethanol, and the precipitated polymer was filtered off. The isolated, polyurea was refluxed under stirring with 500 ml dioxane, filtered again, and dried at 80°C/10^{-1} mbar. Yield, 77%.

ANAL. Calcd for $C_3H_6N_2O_1$: C, 41.85%; H, 7.02%; N, 32.54%. Found: C, 41.21 %; H, 7.32%; N, 32.03%.

Polycondensations with Diphenyl Carbonate

Diphenylcarbonate (21.4 g, 0.1 mole) and 0.1 mole of aliphatic diamine were heated in 150 ml dry dimethylacetamide at 150° C for 8 hr and worked up as described above.

Polycondensations with Diisocyanates

A 50 mmole portion of diamine was dissolved in 150 ml dry dimethylformamide, and a solution of 50 mmole diisocyanate in 20 ml dry dioxane was added under cooling with ice. After 10 min, the reaction mixture was warmed to 100 °C for 4 hr and worked up as described above.

Measurements

The ^{13}C-NMR spectra were obtained on a Bruker WH-90 instrument at a magnetic field strength of 2.1 Tesla (21 Kgauss). Measurements were taken on 400 mg polyurea dissolved in 2 ml trifluoroacetic acid in 10 mm diameter sample tubes with a coaxial 4 mm tube containing a 1:1 mixture (by volume) of dioxane-d_8 and TMS. A pulsewidth of 8.0 μsec (ca. 60°), 8K data points on 5.000 Hz spectral width and an exponential linebroadening of 1.0 Hz was used at 28-30° C.

The 9.12 MHz ^{15}N NMR spectra were obtained on a Bruker WH-90 instrument at ca. 35° C. Measurements were made on 1.5 g polyurea dissolved in 7 ml trifluoroacetic acid in 20 mm diameter sample tubes with a coaxial 5 mm tube containing D_2O and $^{15}NH_4{}^{15}NO_3$. The NO_3^{θ} ion served for shift referencing. A pulse width of 40 μsec (ca. 40°), 1 K data points on 600 Hz spectral width and a line-broadening of 1.0 Hz were used.

The 20.28 MHz ^{15}N NMR spectra were measured on a Bruker WP-200 instrument (4.6 Tesla) with 1 g polyurea dissolved in 5 ml trifluoroacetic acid. Sample tubes of 15 mm diameter with a coaxial 5 mm tube containing D_2O and $^{15}NH_4{}^{15}NO_3$ were used.

It must be emphasized that, if an external standard is used, the chemical shifts obtained with superconducting magnet differ from those obtained with an iron magnet by ca. 1.0-1.5 ppm. For the copolyurea X the following chemical shifts were obtained when measured with the WP-200 instrument (see Fig. 4): -275.69; -276.56, -277.62; 277.91, -278.39, -278.68, -281.90, -282.10, -285.61, -285.80

RESULTS AND DISCUSSION

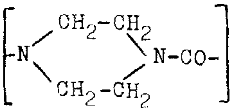
Syntheses

The homopolyureas Ib-d were synthesized from the corresponding diamines and diisocyanates in dry dimethylformamide (DMF) at room temperature. The homopolyureas Ie, If, and II were prepared by aminolysis of diphenylcarbonate in dimethylacetamide at 150° C [Eq. (1)]. In the case of 1,2-diaminoethane this reaction leads to

$$[-NH{-}(CH_2)_n{-}NH{-}CO{-}]$$

Ia-f

Ia:= n = 2
b: n = 3
c: n = 4
d: n = 6
e: n = 8
f: n = 12



II

the formation of a cyclic urea (imidazolidinone-2); furthermore, the isolation of a monomeric ethylene diisocyanate is difficult to achieve. Hence, the polyurea Ia was synthesized from 1,2-diaminoethane and its N-N'-bisphenoxycarbonyl derivative [Eq. (2)], which is easily

$$C_6H_5O{-}CO{-}OC_6H_5 + NH_2{-}(CH_2)_n{-}NH_2 \xrightarrow[-2C_6H_5OH]{} \text{Ic, f} \qquad (1)$$

$$C_6H_5O{-}CO{-}NH{-}(CH_2)_2{-}NH{-}CO{-}OC_6H_5$$

$$+ NH_2{-}(CH_2)_2{-}NH \xrightarrow{150^\circ C}$$

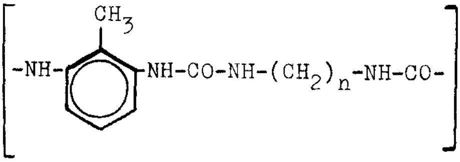
$$\ldots[-NH{-}(CH_2)_2{-}NH{-}CO{-}]\ldots + 2C_6H_5OH \qquad (2)$$

accessible from 1,2-diaminoethane and phenolchloroformate. An aromatic homopolyurea was prepared from 4,4'-diaminodiphenylmethane and 4,4'-diisocyanato diphenylmethane in DMF. However, this polyurea turned out to be insoluble in trifluoroacetic acid and mixtures of this acid with methylene chloride, chloroform or benzene. In methanesulfonic acid, a ^{15}N-NMR spectrum was not obtainable because of signal nulling. Thus, this aromatic homopolyurea was not included in our spectroscopic investigation.

$$[-NH-(CH_2)_6-NH-CO-NH-(CH_2)_n-NH-CO-]$$

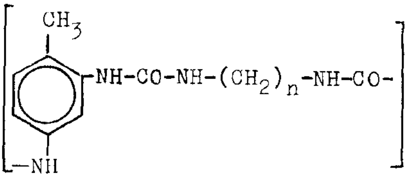
IIIa-f

IIIa: n = 2
b: n = 3
c: n = 4
d: n = 6
e: n = 8
f: n = 12

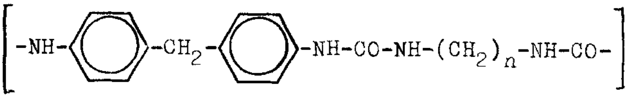


IVa-c

IV, V a: n = 2
b: n = 3
c: n = 6



Va-c



VI a-e

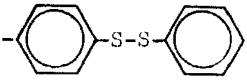
VI a: n = 2
b: n = 3
c: n = 4
d: n = 6
e: n = 12

$[-NH-(CH_2)_6-NH-CO-NH-A-NH-CO-]$

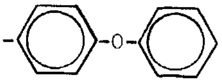
VII a-c

VIIa: A =

b: A =



c: A =



Two kinds of copolyureas were synthesized, namely polyureas with an alternating sequence of two different diamines (IIIa-f, IVa-c, Va-c, VIa-d, VIIa-c) and polyureas with a random sequence. All these copolyureas were obtained from the reaction of diamines with diisocyanates. The following random copolyureas were prepared: VIII: from 1,3-diaminopropane, 1,3-diaminobenzene, and 1,6-hexamethylene diisocyanate (Table 2); IX: from 1,3-diaminopropane, 1,6-diaminohexane, 1,3-diaminobenzene, and 1,6-hexamethylene diisocyanate (Table 2); X: from 1,3-diaminopropane, 1,6-diaminohexane, 2,6-toluylene diisocyanate, and 2,4-toluylene diisocyanate (Figs. 2 and 4 and Table 1).

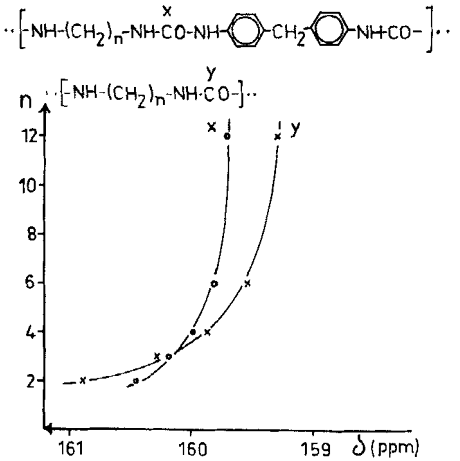


FIG. 1. ^{13}C-NMR chemical shifts δ (downfield of external TMS) of the carbonyl signal of polyureas in trifluoroacetic acid.

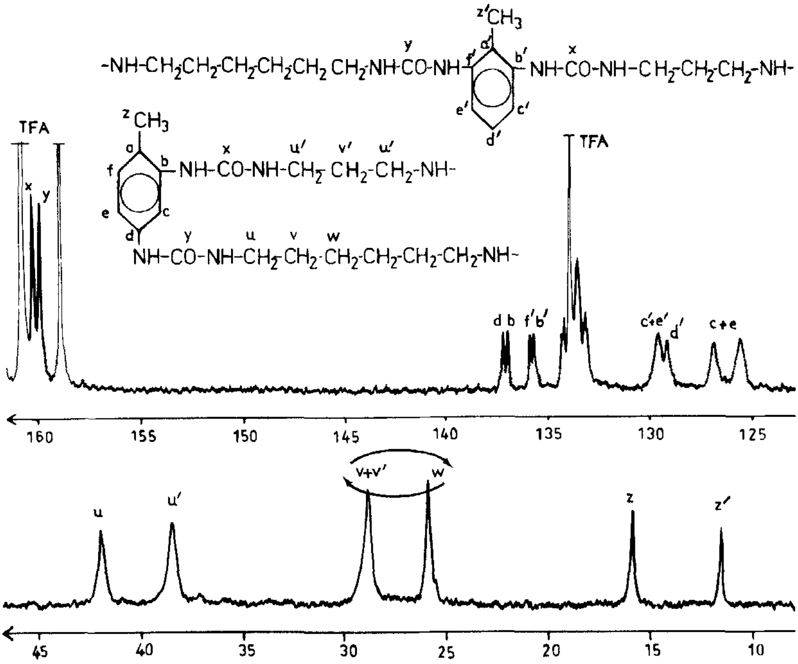


FIG. 2. 22.63 MHz ^{13}C-NMR spectrum of a copolyurea in trifluoroacetic acid prepared from 1,3-diaminopropane, 1,6-diaminohexane (mole ratio 1:1), 2,6-toluylene diisocyanate, and 2,4-toluylene diisocyanate (mole ratio 1:1.5), (x).

^{13}C-NMR Spectroscopy

The ^{13}C-NMR spectra and the ^{15}N-NMR spectra were measured in trifluoroacetic acid (TFA), because TFA is a good solvent not only for polyureas, but also for polyamides and polyurethanes, so that a direct comparison of the chemical shifts of all these various classes of polymers becomes possible. The relatively low viscosity of TFA favors a small line width of the signals as well as a strong, negative nuclear Overhauser effect, in the case of the ^{15}N-NMR signals. Furthermore, we observed phase separation when polyureas were dissolved in mixtures of TFA with methylene chloride, chloroform, or chlorobenzene, although such mixtures are good solvents for aliphatic polyamides, polyurethanes, and polyesters. Most polyureas were not soluble in formic acid or formic acid/methylene chloride mixtures. In methanesulfonic acid, which is a good solvent for polyureas, signal nulling was observed in the case of the ^{15}N-NMR measurements because of an unfavorable nuclear Overhauser effect.

TABLE 1. ^{13}C-NMR Chemical Shifts δ of Polyureas in Trifluoroacetic Acid

Polyurea		δ (ppm downfield from TMS)		
Formula	Components	CO	α-C	Other carbons
Ia	1,2-Diaminoethane	160.89	41.00	
Ib	1,3-Diaminopropane	160.27	39.00	28.35
Ic	1,4-Diaminobutane	159.86	41.54	25.74
Id	1,6-Diaminohexane	159.50	42.19	25.96 28.54
Ie	1,12-Diaminododecane	159.32	42.35	26.33 28.59; 28.92[a]
II	Piperazine	162.13	46.99	
IIIa	1,2-Diaminoethane	160.24	41.00	
	1,6-Diaminohexane		42.19	26.00 28.38
IIIb	1,3-Diaminopropane	159.81	38.96	28.38
	1,6-Diaminohexane		42.19	26.00 28.38
IIIc	1,4-Diaminobutane	159.65	41.54	25.90
	1,6-Diaminohexane		42.19	25.90 28.38
IIIe	1,8-Diaminooctane	159.44	42.35	26.33 28.54; 28.76
	1,6-Diaminohexane		42.19	25.95 28.54
IIId	1,12-Diaminododecane	159.38	42.40	26.38 28.54; 28.92;[a] 29.24
	1,6-Diaminohexane		42.10	25.90 28.54
IVa	1,2-Diaminoethane	160.57	41.00	
	2,6-Diaminotoluene		135.37	134.35 129.22;[b] 128.73; 11.65
IVb	1,3-Diaminopropane	160.30	38.63	29.19
	2,6-Diaminotoluene		135.69	134.18 129.53;[b] 129.00; 11.60

IVc	1,6-Diaminohexane	159.86	42.03	25.95 28.92
	2,6-Diaminotoluene		135.91	133.86 129.70;[b] 129.06; 11.56
Vb	1,3-Diaminopropane	160.24	38.58	28.97
	2,4-Toluylendiamine		136.88	133.48; 126.88; 125.54; 15.97
Vc	1,6-Diaminohexane	159.76	42.03	25.90; 28.76
	2,4-Toluylendiamine		137.15	133.05; 127.77; 125.77; 15.86
VIa	1,2-Diaminoäthane	160.46	40.68	
	4,4-Diaminodiphenylmethane		142.38	131.32; 130.95; 126.36;[b] 40.68
VIb	1,3-Diaminopropane	160.19	38.63	28.76
	4,4'-Diaminodiphenylmethane		142.60	131.11; 126.52;[b] 40.63
VIc	1,4-Diaminobutane	159.97	41.49	26.06
	4,4'-Diaminodiphenylmethane		142.71	131.11; 126.57;[b] 40.68
VId	1,6-Diaminohexane	159.81	42.14	25.86; 28.75
	4,4'-Diaminodiphenylmethane		142.65	131.05; 126.57;[b] 40.63
VIe	1,12-Diaminododecane	159.72	42.30	26.45; 28.76; 28.98[a]
	4,4'-Diaminodiphenylmethane		142.60	131.02; 126.57;[b] 40.61
VIIb	1,6-Hexamethylenediamine	159.06	42.19	25.95; 28.65
	4,4'-Diaminodiphenylenedisulfide		138.39	132.29; 128.84; 126.63

(continued)

TABLE 1 (continued)

Polyurea		δ (ppm downfield from TMS)		
Formula	Components	CO	α-C	Other carbons
X	1,3-Diaminopropane	160.24	38.52	28.86
	1,6-Diaminohexane		42.08	28.86; 25.90
			135.80	
	2,6-Diaminotoluene	159.86	135.68	134.07; 129.65; 129.11; 11.55
	2,4-Diaminotoluene		137.15	133.43; 126.95; 125.60; 15.92
			136.94	

[a] Signal represents four carbons.

[b] Carbons in 3,5-position (ortho to the nitrogens).

TABLE 2. ^{15}N-NMR Chemical Shifts δ of Various Polyureas in Trifluoroacetic Acid

Structure	Polyurea of	δ (ppm, upfield of external $NO_3^{\ominus}$)[a]
Ia	1,2-Diaminoethane	-292.6
Ib	1,3-Diaminopropane	-289.4
Ic	1,4-Diaminobutane	-287.6
Id	1,6-Diaminohexane	-287.0
Ie	1,8-Diaminooctane	-286.8
If	1,12-Diaminododecane	-286.6
IIIa	1,2-Diaminoethane 1,6-Diaminohexane	-293.5 -285.5
IIIb	1,3-Diaminopropane 1,6-Diaminohexane	-290.0 -286.0
IIIc	1,4-Diaminobutane 1,6-Diaminohexane	-288.3 -286.7
IIIe	1,8-Diaminooctane 1,6-Diaminohexane	-287.2 -286.6
IIIf	1,12-Diaminododecane 1,6-Diaminohexane	-287.4 -286.5
IVa	1,2-Diaminoethane 2,6-Diaminotoluene	-290.1 -278.3
IVb	1,3-Diaminopropane 2,6-Diaminotoluene	-286.8 -278.6
IVc	1,6-Diaminohexane 2,6-Diaminotoluene	-283.2 -279.4
Va	1,6-Diaminohexane 2,4-Diaminotoluene	-282.9 -280.6 -277.8
VIa	1,2-Diaminoethane 4,4'-Diaminophenylmethane	-290.7 -275.1
VIb	1,3-Diaminopropane 4,4'-Diaminophenylmethane	-287.0 -276.1
VIc	1,4-Diaminobutane 4,4'-Diaminodiphenylmethane	-284.9 -276.6
VId	1,6-Diaminohexane 4,4'-Diaminodiphenylmethane	-283.8 -277.0

(continued)

TABLE 1 (continued)

Structure	Polyurea of	δ (ppm, upfield of external NO_3^{θ})[a]
VIe	1,12-Diaminodudecane	-283.2
	4,4'-Diaminodiphenylmethane	-277.2
VIIa	1,6-Diaminohexane	-282.7
	1,4-Diaminobenzene	-277.2
VIIb	1,6-Diaminohexane	-283.4
	4,4'-Diaminodiphenylene disulfide	-277.4
VIIc	1,6-Diaminohexane	-283.6
	4,4'-Diaminophenylene oxide	-278.0
VIII	1,3-Diaminopropane	-290.1
	1,6-Diaminohexane	-286.1
	1,3-Diaminobenzene	-282.7
		-276.6
IX	1,3-Diaminopropane	-290.1
	1,6-Diaminohexane	-287.0
	1,3-Diaminobenzene	-286.1
		-282.7
		-276.7

[a] Measured with a Bruker WH-90 instrument at 9.12 MHz in 20 mm sample tubes.

Thus, TFA was found to be the most useful solvent for both ^{13}C- and ^{15}N-NMR spectroscopy, although in the ^{13}C-NMR spectra a partial overlapping of solvent and solute signals was observed in some cases (Fig. 2).

In analogy with polyamides [2, 5] and polyesters [1], the carbonyl-signals of aliphatic polyureas are sensitive to the chain length of the monomer units. However, in contrast to polyamides and polyesters the shift effects caused by different chain length is small ($\Delta\delta_{max} \sim$ 1.6 ppm) (Fig. 1) and its direction is opposite. Increasing chain length leads to an upfield shift in contrast to the downfield shift observed for other polymers (Fig. 1). We have explained the downfield shift/chain length relationships of polyamides and polyesters by two arguments: (a) increasing chain length enhances the basicity of amide and ester groups leading to stronger H-bonds and protonation in acidic solvents; and (b) the methylene groups cause direct substituent effects similar to β- and δ-carbons in branched aliphatic systems [13, 14]. The first argument is probably not useful in the case of polyureas, because their basicity is high enough to allow a nearly complete protonation in TFA, even in the case of short monomer units. However, the second argument should hold for all aliphatic chains; thus, the spectroscopic behavior of the polyureas presents an unexpected feature which we cannot explain at the current stage of our investigation. In favorable cases, the carbonyl signals allow one to distinguish an alternating sequence, e. g., IIId, from a mixture of the corresponding homopolymers (Ia and Id) and from a random sequence which must display three carbonyl signals. However, the small shift differences severely limit the application of this method.

Also in the case of aromatic polyureas, the carbonyl signals are rather sensitive to neighboring residue effects. For example the carbonyl groups of polyureas containing 2,6-toluylenediamine or 4,4'-diaminodiphenylmethane have nearly identical shifts, provided that the second component of the polymer is identical (Table 1). Thus, it is not surprising that the urea groups of 2,4-toluylenediamine-containing polymers cannot be distinguished from each other. On the other hand, the quaternary carbons bound to the urea groups exhibit unexpected long range effects, because their chemical shifts are influenced by the chain length of the aliphatic monomer units (Table 1 and Figs. 2). These shift effects are obviously small and are not reliable guides for a NMR sequence analysis.

^{15}N-NMR Spectroscopy

When the homopolyureas I a-f were measured in trifluoroacetic acid a distinct shift/structure relationship was found. Increasing chain length of the aliphatic diamine results in a downfield shift of the ^{15}N signal (Table 2). Because no irregular substituent effects such as γ- or δ-effects are found and since the influence of each additional CH_2 group decreases with increasing chain length, the chemical shift/chain length-relationship is an exponential function (Fig. 3, curve 2). Similar relationships were found when the ^{15}N-NMR chemical shifts of polyamides were plotted versus the chain length of the monomeric units [7]. A new aspect comes into sight, when the chemical shifts of the alternating copolyureas IIIa-f are compared with those of the homopolymer I a-f (Fig. 1), because the shifts of identical monomeric units (diamines) are not identical in the two classes of polyureas (Fig. 3 and Table 2). This observation demonstrates that neighboring residue effects exist, so that a monomer unit not only influences the shift of the directly attached two nitrogens but also the shifts of the neighboring residues (see Fig. 4). These neighboring residue effects are not only found in when aliphatic copolyureas are measured, they are also observable in the case of aromatic copolymers such as IVa-c or VI a-f (see Table 2 and Fig. 5). The existence of these neighboring residue effects renders ^{15}N-NMR spectroscopy a valuable method for the characterization of copolyureas.

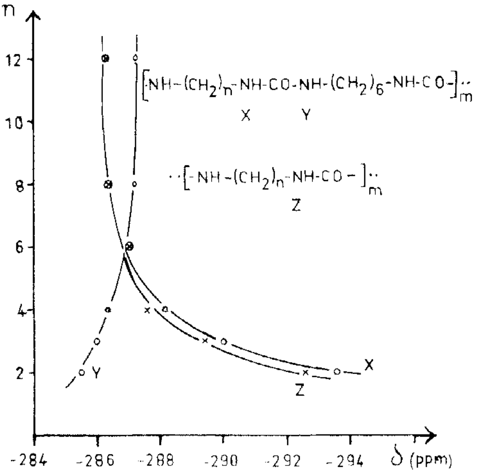


FIG. 3. ^{15}N-NMR chemical shifts δ (upfield of external $NO_3^{\ominus}$) of aliphatic homo- and copolyureas measured at 9.12 MHz in trifluoroacetic acid.

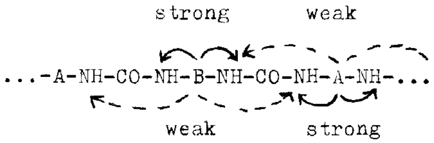


FIG. 4. Scheme of neighboring residue effects in the ^{15}N-NMR spectra of copolyureas.

If, for example, 4,4'-diaminodiphenylene oxide is reacted with 1,6-hexamethylene diisocyanate in dry DMF, the resulting polyurea exhibits in its ^{15}N-NMR spectrum only two signals corresponding to the alternating sequence VIIc (Table 2). The same reaction carried out in moist DMF leads to a polyurea with an additional signal of weak intensity (δ = -287.1 ppm), steming from urea groups which link two 1,6-diaminohexane units. In moist DMF, water can compete with the poorly nucleophilic aromatic diamine in attacking the diisocyanate. The hydrolysis, then, leads to the formation of 1,6-diaminohexane, which in turn reacts fast with 1,6-hexamethylene diisocyanate, whereby the additional urea group is formed. Furthermore, the copolyureas VIII and IX demonstrate that by means of ^{15}N-NMR spectra it is possible to distinguish polyureas built up by identical monomer units, but prepared in different ways. IX contains three different urea

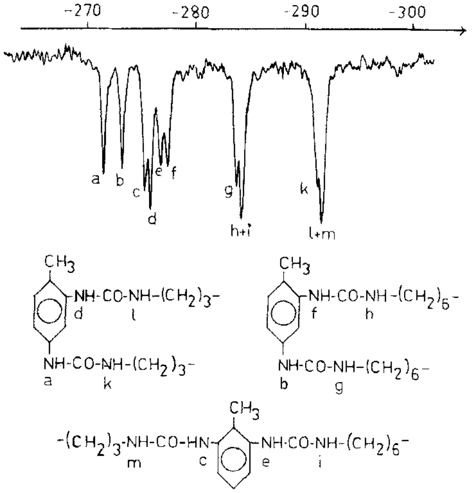


FIG. 5. Natural abundance 20.26 MHz ^{15}N-NMR spectrum of a copolyurea (in TFA) obtained by conversion of a 1:1 mixture of 1,3-diaminopropane and 1,6-diaminohexane with a 1.5:1 mixture of 2,4-toluylene diisocyanate and 2,6-toluylene diisocyanate, (x).

groups, one linking two identical monomer units (1,6-diaminohexane) and two linking different monomer units. Thus, five signals are observable, while the two different, alternating urea groups of VIII give rise to four signals. Finally it should be pointed out that polyureas derived from 2,4-toluylene diisocyanate show a shift difference of ca. 3 ppm for the 2- and 4-nitrogens. Moreover, the 2-urea group of 2,4-toluylene diamine is distinguishable from that of 2,6-toluylenediamine, so that it is easy to identify the individual urea groups in copolymer X (Table 2 and Fig. 5).

Scheme of ^{15}N-NMR Sequence Analysis

The general validity of the neighboring residue effects demonstrated in Figs. 3-5 allows one to calculate the maximum number of signals (MNS) which may be found in the ^{15}N-NMR spectrum of copolyureas. This maximum number of ^{15}N-NMR signals (MNS) not only depends on the number of different monomer units (diamines), but also on the way of synthesis. Thus, for a copolyurea built up by two different monomer units the MNS is 2, if the copolyurea is prepared from one diisocyanate and one diamine; MNS = 3, it if is prepared from one diisocyanate and two diamines or from two diisocyanates and one diamine; MNS = 4, if it is prepared from two diisocyanates and two diamines. For a copolyurea with three different monomer units, MNS = 4, if it is prepared from one diisocyanate and two diamines or from two diisocyanates and one diamine; MNS = 5, if it is prepared from one diisocyanate and three diamines or from one diamine and three diisocyanates; MNS = 8, if it is prepared from two diisocyanates and three diamines or from three diisocyanates and two diamines; MNS = 9, if it is prepared from three diisocyanates and the corresponding three diamines.

Analogous calculations can be carried out for copolyureas built up by four or more different monomer units. In addition to the synthesis from diamines and diisocyanates, copolyureas can be prepared from mixtures of diamines and phosgene or its substitutes (e. g., carbonyl diimidazole or diphenylcarbonates). This synthesis route leads to random sequences with a MNS equal to n^2, where n is the number of different diamines. Unsymmetrical diamines, such as p-aminobenzylamine or unsymmetrical diisocyanates, such as toluylene 2,4-diisocyanate, behave with respect to the MNS like a 1:1 mixture of two symmetrical diamines or diisocyanates respectively (Fig. 5). Whether the MNS is really resolved in the ^{15}N-NMR spectrum of copolyurea depends, of course, on the strength of the neighboring residue effects and on the quality of the NMR spectrometer.

Finally, it must be emphasized that a quantitative evaluation of the signal intensities for the calculation of block length or reactivity ratios [15] is not possible if broadband ^{1}H-decoupling is applied as in Fig. 5. Since the nuclear Overhauser effect (NOE) is dependent on the segmental mobility of the individual urea groups, the "inverse-gated ^{1}H-decoupling" technique must be applied to eliminate the NOE.

CONCLUSION

Our systematic NMR spectroscopic investigation of various aliphatic and aromatic polyureas demonstrates that ^{13}C-NMR spectra are rather useless for identifying individual urea groups. The ^{15}N-NMR signals of urea groups, on the other hand, are so sensitive to the nature of substituents that they allow the sequence analysis of copolyureas. A comparison of the ^{15}N-NMR shifts of urea groups with those of amide groups [7], furthermore, demonstrates that their distinction in copolymers does not present any problem. A paper dealing with the identification of urea groups in polyurethanes will be presented elsewhere. However, it must be emphasized that natural abundance ^{15}N-NMR spectra have the general drawback of a low signal-to-noise ratio, so that the detection of low concentration of urea groups is difficult.

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