Poly(amidourethane)s with regular sequence of amide and urethane groups

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A number of diamidodiisocyanates and trimethylsiloxyalkylamidoisocyanates were synthesized by regioselective reaction of isocyanatoalkanoyl chlorides and trimethylsilyldiamines or trimethylsilylamino-alcohols. They were converted to poly(amidourethane)s with regular structure, whose thermal behaviour was investigated in relation to their structure and compared with corresponding polyamides.

(Keywords: poly(amidourethane)s; synthesis, thermal behaviour)

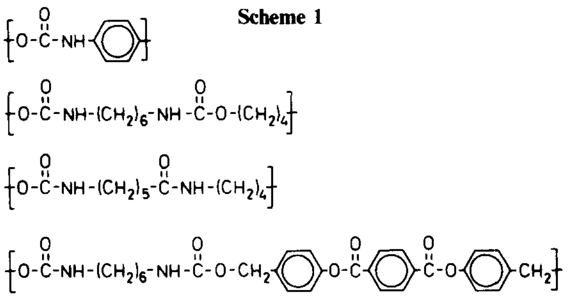
INTRODUCTION

Progress in polymer chemistry and improvement of polymer performance are directed to more sophisticated methods of polymerization and the design of polymers with higher differentiation and organization of the chain (long constitutional units, substituents with special properties). Main-chain liquid crystals are probably the most impressive example of this development. Most of them can be regarded as copolymers having a regular sequence of several base units (sequential copolymers)[1].

Sequential copolymers are usually made by step-growth polymerization reactions of difunctional intermediates which contain the desired structural elements and suitable functional groups. This also requires improved synthetic methods for new monomers or intermediates.

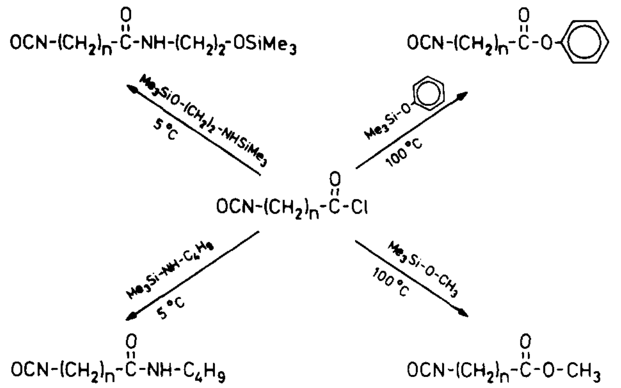
Analogous products with isocyanate end-groups could be useful for the synthesis of sequential polyurethane copolymers. They enable the properties of the resulting polymers to be tailored without losing the regular structure and the advantages of polyurethane technology. Up to now, polyurethanes have been reported in the literature which are derived from a hydroxyalkyl- or hydroxyarylisocyanate[2] (comparable to the Perlon series of polyamides) and from a diisocyanate and a diol (in analogy to the nylon series), and there are a few examples of sequential copolymers based on diol intermediates[3]. Poly(amidourethane)s with a strictly alternating sequence have not been described.

Scheme 1



The regioselective reaction of isocyanatoacyl chlorides with silyl-protected hydroxy and amino compounds to form isocyanatocarboxylic acid esters and amides is a convenient and versatile method for the design of isocyanate intermediates in high yields[4]. Ester-group-containing diisocyanates are made at higher temperatures and can be catalysed by Lewis acids and bases. The analogous reaction with *N*-trimethylsilylamines proceeds at low temperature without the need for a catalyst. This difference in reaction conditions enables a further regioselective reaction of an isocyanatoalkanoyl chloride with an *O*,*N*-bis(trimethylsilyl)aminoalcohol to give *N*-(trimethylsiloxyalkyl)isocyanatocarboxamides.

Scheme 2



The development of a general synthesis of trimethylsiloxyalkyl- and trimethylsiloxyarylisocyanates[5] completes the kit for tailoring ester-group-containing diisocyanates.

Synthesis of aliphatic diisocyanato esters[6], of mesogenic aromatic–aliphatic diisocyanato esters[7] and of liquid-crystalline diad as well as triad diisocyanato esters[8] and their polyaddition to polyurethanes have been described.

The present paper deals with the synthesis of diisocyanatodicarboxamides, *N*-(trimethylsiloxyalkyl)isocyanatocarboxamides and their reaction to sequential poly(diamidodiurethane)s and strictly alternating poly(amidourethane)s.

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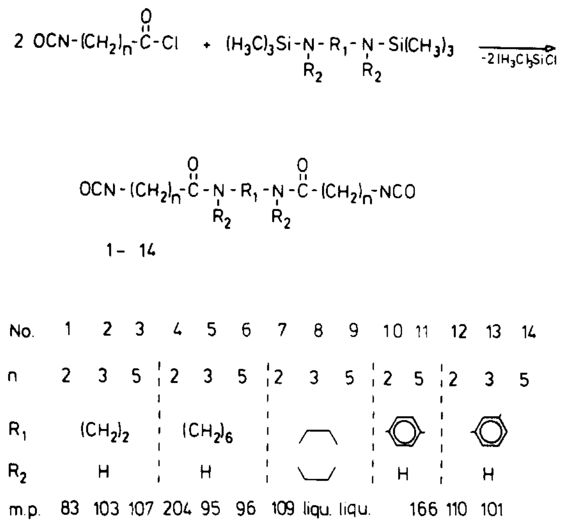
RESULTS AND DISCUSSION

Synthesis of isocyanatocarboxamides

Isocyanatocarboxamides which to our knowledge had not been described in the literature as isolated pure products[9] were made as outlined above.

The isocyanatoacyl chlorides used in this work were isocyanatopropanoyl, -butanoyl and -hexanoyl chlorides (**1–3**)[10]. The *N,N'*-bis(trimethylsilyl)diamines were chosen as examples of aliphatic diamines with different chain lengths (1,2-diaminoethane, 1,6-diaminohexane), of a secondary aliphatic diamine (piperazine) and of aromatic diamines with different substitution patterns (*m*- and *p*-phenylenediamine).

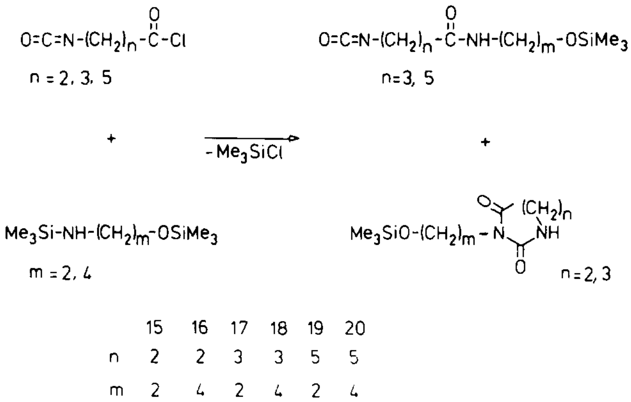
Scheme 3



No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
n	2	3	5	2	3	5	2	3	5	2	5	2	3	5
R_1	$(CH_2)_2$			$(CH_2)_6$										
R_2	H			H						H		H		
m.p.	83	103	107	204	95	96	109	liqu.	liqu.		166	110	101	

2-Aminoethanol and 4-aminobutanol were used for the synthesis of *N*-(trimethylsiloxy)isocyanatocarboxamides (**15–20**).

Scheme 4



	15	16	17	18	19	20
n	2	2	3	3	5	5
m	2	4	2	4	2	4

Silylation was made by heating equimolar amounts of the diamines and hexamethyldisilazane[11]. The regioselective reactions of the silylated amines with the isocyanatoalkanoyl chlorides were made in toluene at temperatures below 5°C in order to avoid reaction of the isocyanate group which is possible at higher temperatures with reactive isocyanates[12].

The desired diisocyanatodicarboxamides separated as colourless powders from the reaction mixture. The products **8**, **9** and **14** did not crystallize, but separated as liquids or gave a brittle resinous material (**14**) after removal of solvent. The crystalline diisocyanatodicarboxamides which were obtained almost analytically pure could be further purified by recrystallization from ethyl acetate; the others were used as obtained, because they could not be distilled without decomposition and gave elemental analyses and i.r. as well as n.m.r. spectra in good agreement with the proposed structure. The melting points of the diisocyanatodicarboxamides are added in *Scheme 3*; for complete analytical and spectroscopic data, see ref. 13.

The *N*-(trimethylsiloxyalkyl)isocyanatoacylamides are soluble in toluene and obtained as colourless liquids after short-path distillation. They gave correct microanalyses without further purification. The infra-red spectra show characteristic absorptions at 3300 (N–H stretching), 2280 (N=C=O), 1690–1630 (amide I) and 1560–1535 cm^{-1} (amide II) except for the 3-isocyanatopropanamides, where the isocyanate absorption has disappeared and a new carbonyl absorption appears at 1720 cm^{-1}. The analytical data are summarized in *Table 1*.

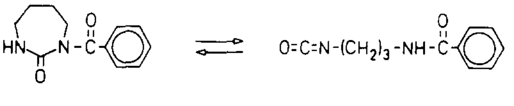
The bis-3-isocyanatopropanamides from primary diamines (**1**, **4**, **10** and **12**) are obviously the primary reaction products, which however are not stable in solution or at higher temperatures. The soluble products and the insoluble compounds after heating in boiling xylene have no isocyanate absorption in the i.r. spectrum but an additional carbonyl absorption at 1720 cm^{-1} instead. Cyclization occurs under these conditions and 3-substituted 5,6-dihydropyrimidinediones are formed by intramolecular attack of the isocyanate on the amide nitrogen (*Scheme 4*). The formation of dihydrouracils by reaction of **2** with primary amines has been described by Kricheldorf[14].

The pyrimidinediones proved to be almost nonreactive with alcohols in boiling *o*-dichlorobenzene and hence were left apart for the polyaddition reactions.

A similar behaviour was observed with the *N*-(trimethylsiloxyalkyl)-4-isocyanatobutanamides (*Scheme 4*). They are stable at room temperature but cannot be distilled without partial cyclization to seven-membered ring acylureas (1,3-diazacyclohepta-2,4-diones). Prolonged heating to temperatures of 180°C effected complete cyclization. *Figure 1* shows the infra-red spectra of *N*-(4-trimethylsiloxybutyl)-4-isocyanatobutanamide (**18**) and its cyclization product.

Ulrich and coworkers synthesized isomeric seven-membered ring acylureas which were converted into the corresponding amidoisocyanates in boiling *o*-dichlorobenzene[15].

Scheme 5



Temperature-dependent i.r. spectra of **18a** indicated a similar behaviour, although the intensity of the isocyanate absorption had a maximum at about 130°C, which is in agreement with its formation at high temperatures (*Figure 2*).

Sequential poly(diamidodiurethane)s

The diamidodiisocyanates described above were reacted

Table 1 Characteristic properties of *N*-(trimethylsiloxyalkyl)isocyanatoalkanamides

No.	Yield (%)	B.p.[a] at 10^{-4} mbar (°C)	Molecular formula[b]	I.r. (cm^{-1})	^1H n.m.r. in $CDCl_3$ (ppm)
15[c]	81	130 (48.5)[d]	$C_9H_{18}N_2O_3Si$	3300, 1720, 1665	0.10(s,9H), 2.72(t,2H), 3.39(q,2H), 3.80(m,4H), 5.65(s,1H)
16[c]	74	160 (52)[d]	$C_{11}H_{22}N_2O_3Si$	3300, 1715, 1665	0.10(s,9H), 1.61(m,4H), 2.74(t,2H), 3.60(m,6H), 5.95(s,1H)
17	84	180	$C_{10}H_{20}N_2O_3Si$	3300, 2280, 1665	0.08(s,9H), 1.86(m,2H), 2.21(t,2H), 3.30(m,4H), 3.72(t,2H), 5.95(s,1H)
17a[e]	-	210	$C_{10}H_{20}N_2O_3Si$	3300, 1710, 1540	0.08(s,9H), 1.87(m,2H), 2.20(t,2H), 2.55(m,2H), 3.31(t,2H), 3.72(t,2H), 6.21(s,1H)
18	quant.	190	$C_{12}H_{24}N_2O_3Si$	3300, 2280, 1650, 1550	0.02(s,9H), 1.47(m,4H), 1.87(m,2H), 2.17(t,2H), 3.21(m,4H), 3.41(t,2H), 6.21(s,1H)
18a[e]	-	205	$C_{12}H_{24}N_2O_3Si$	3300, 1705, 1530	0.06(s,9H), 1.57(m,4H), 2.02(m,2H), 2.56(m,2H), 3.26(m,2H), 3.56(t,2H), 3.80(t,2H), 8.38(s,1H)
19	89	200	$C_{12}H_{24}N_2O_3Si$	3300, 2280, 1654, 1550	0.03(s,9H), 1.49(m,6H), 2.18(t,2H), 3.15(m,4H), 3.58(t,2H), 6.06(s,1H)
20	86	205	$C_{14}H_{28}N_2O_3Si$	3300, 2280, 1650, 1550	0.03(s,9H), 1.48(m,10H), 2.10(t,2H), 3.20(m,4H), 3.52(t,2H), 6.05(s,1H)

[a] Temperature of heating cylinder of glass tube oven (Büchi)
[b] Correct microanalyses obtained for all compounds
[c] Subst. 5,6-dihydropyrimidine-2,4-diones
[d] Melting point
[e] Subst. 1,3-diazacyclohepta-2,4-diones

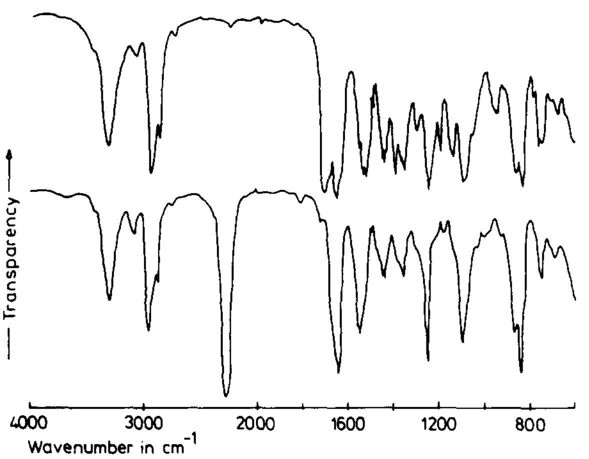


Figure 1 I.r. spectra of *N*-(4-trimethylsiloxybutyl)-4-isocyanatobutanamide **18** (lower curve) and its cyclization product 3-(4-trimethylsiloxybutyl)1,3-diazacyclohepta-2,4-dione **18a** (upper curve)

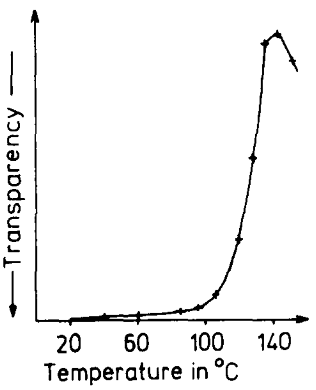
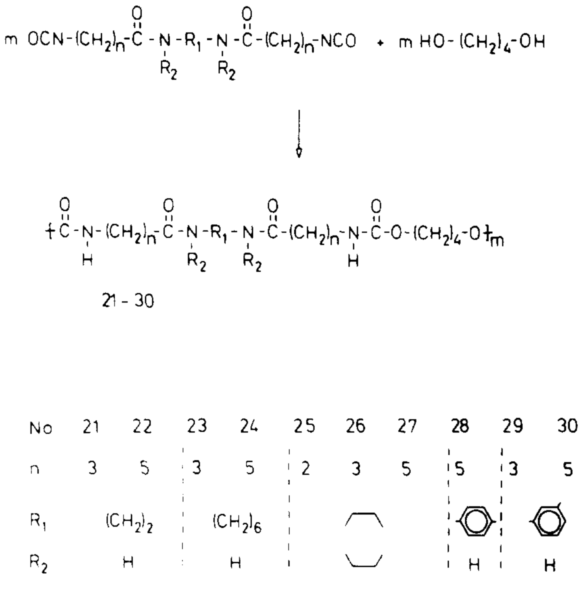


Figure 2 Temperature dependence of the isocyanate absorption (ring chain equilibrium) of **18a**

with 1,4-butanediol to poly(diamidodiurethane)s with regular sequence.

Scheme 6



$$m\,OCN-(CH_2)_n-\overset{O}{\overset{\|}{C}}-\underset{R_2}{N}-R_1-\underset{R_2}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_n-NCO + m\,HO-(CH_2)_4-OH$$

$$\downarrow$$

$$\left[\overset{O}{\overset{\|}{C}}-\underset{H}{N}-(CH_2)_n-\overset{O}{\overset{\|}{C}}-\underset{R_2}{N}-R_1-\underset{R_2}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_n-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-O\right]_m$$

21 - 30

The polyaddition reactions were made in dimethylacetamide without the use of a catalyst until the isocyanate groups had reacted (i.r. control). The polymers were isolated by precipitation in methanol. The properties of the poly(diaminodiurethane)s are summarized in *Table 2*, and selected d.s.c. traces are shown in *Figure 3*.

The inherent viscosities of the poly(diamidodiurethane)s are in the range of 0.2 and 0.7 dl g^{-1}. Polymers **21–24** and **28–30** with secondary amide moieties have melting points between 165 and 205°C, which is of the

Table 2 Composition and properties of poly(diamidodiurethane)s

No.	Isocyanate	Yield (%)	Reaction Solv.	Reaction Temp. (°C)	M.p.[a] (°C)	η_{inh}[b] ($dl g^{-1}$)	I.r.
21	**2**	89	DMA	80	204	0.24	*c*
22	**3**	95	DMA	80	192	0.18	*c*
23	**5**	89	DMA	80	183	0.17	*c*
24	**6**	82	DMA	80	165	0.26	*c*
25	**7**	68	DMA	80	116	0.32	*c*
26	**8**	79	DMA	80	117	0.24	*c*
27	**9**	84	DMA	80	141	0.30	*c*
28	**11**	81	DMA	80	dec.	0.73	*c*
29	**13**	77	DMA	80	–	0.18	*c*
30	**14**	81	DMA	80	–	0.20	*c*

[a] From d.s.c. (peak maximum)
[b] In DMA (25°C) at a concentration of $0.3 g dl^{-1}$
[c] I.r. (all polymers): 3330–3350, 1690–1700, 1640–50, $1540 cm^{-1}$

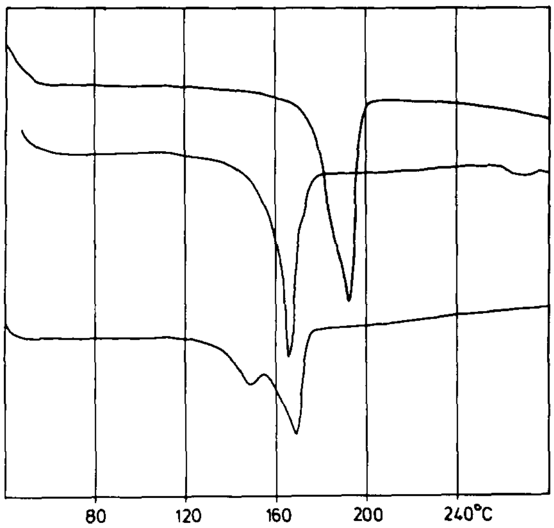


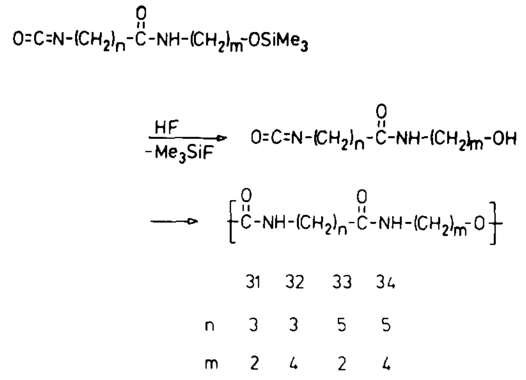
Figure 3 D.s.c. traces of poly(diamidodiurethane)s **22** (upper curve), **24** (middle curve) and **27** (lower curve) at heating rate $20°C min^{-1}$

order of that of the polyurethane made from hexamethylenediisocyanate and 1,4-butanediol. The melting temperatures depend in the expected way on the length of the diamine and of the carboxylic acid (mean distance of the hydrogen bonds in the chain). Tertiary amide groups, which cannot act as hydrogen-bond donors (**25–27**) have melting points of about 120°C—the same level as is observed with poly(diesterdiurethane)s[5]. Aromatic poly(diamidodiurethane)s **28–30** do not melt without decomposition; the *m*-phenylenediamine products **29** and **30** show some softening at about 150°C but no melting endotherm in the d.s.c. trace. The aliphatic polymers are soluble in *m*-cresol and in hot dimethylformamide, and all compounds in dimethylformamide/5% LiCl.

Alternating poly(amidourethane)s

Desilylation of the *N*-(trimethylsiloxyalkyl)isocyanatoalkanoylamides to *N*-hydroxyalkylamidoisocyanates and simultaneous or subsequent polyaddition yielded the strictly alternating poly(amidourethane)s.

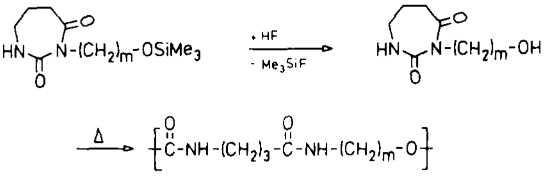
Scheme 7



Desilylation could be made best with hydrogen fluoride/pyridine in the presence of dibutyltin dilaurate as catalyst for the urethane formation. The poly(amidourethane)s **31–34** thus obtained have inherent viscosities between 0.15 and $0.25 dl g^{-1}$. The characteristic properties are shown in *Table 3*. I.r., n.m.r. spectra and correct microanalyses support the alternating character of the new products. *Figure 4* shows the n.m.r. spectra of the monomer **20** and its poly(amidourethane) **34**.

The cyclic diazepinedione gave an oligomeric product when subjected to this procedure. When it was heated to 200°C (molten state) a polymer was obtained which had the same properties as the one prepared from the open-chain isomer **32**.

Scheme 8



The alternating poly(amidourethane)s are crystalline materials with melting points around 200°C (*Figure 5*). In *Table 4* the melting points of the poly(amidourethane)s are compared with those of the corresponding polyamides[16,18]. They are in the same order if the polyamides

Table 3 Characteristic properties of alternating poly(amidourethane)s

No.	Isocyanate	Yield (%)	M.p.[a] (°C)	η_{inh}[b] (dl g^{-1})	I.r. (cm^{-1})
31	**17**	77	190–196 (195)	0.16	3300, 1695, 1654, 1545
32	**18**	77	194–197 (197)	0.22	3300, 1700, 1650, 1540
32a	**18**	73	194–197 (196)	0.20	3300, 1700, 1650, 1545
33	**19**	82	198–204 (199)	0.25	3300, 1700, 1650, 1540
34	**20**	88	199–204 (201)	0.26	3300, 1690, 1645, 1540

[a] Numbers in brackets from d.s.c. (peak maximum)
[b] In *m*-cresol at 25°C, 0.3 g dl^{-1}

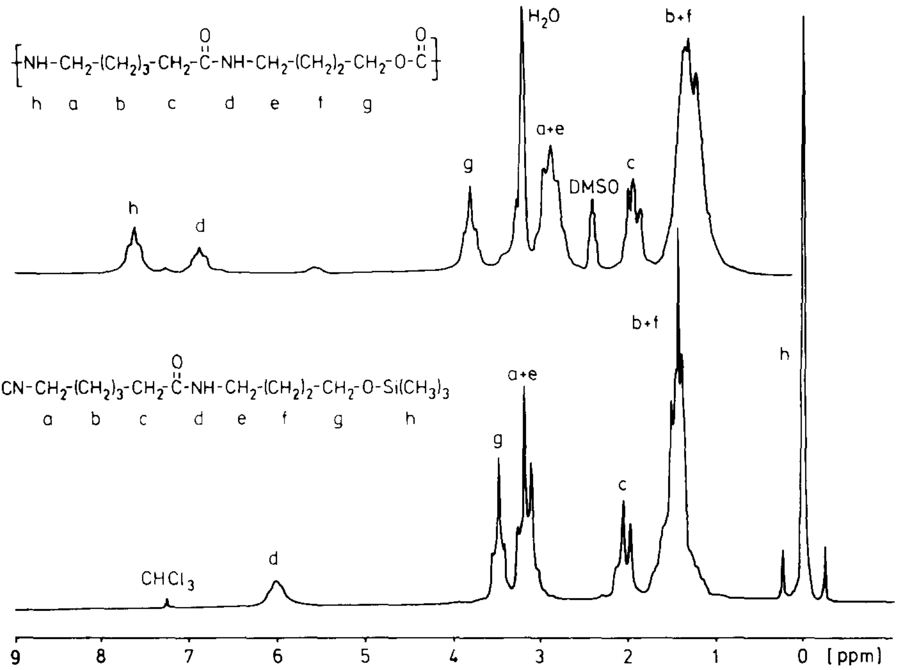


Figure 4 Proton n.m.r. of *N*-(4-trimethylsiloxybutyl)-6-isocyanatohexanamide **20** (lower curve) and its polymer **34** (upper curve)

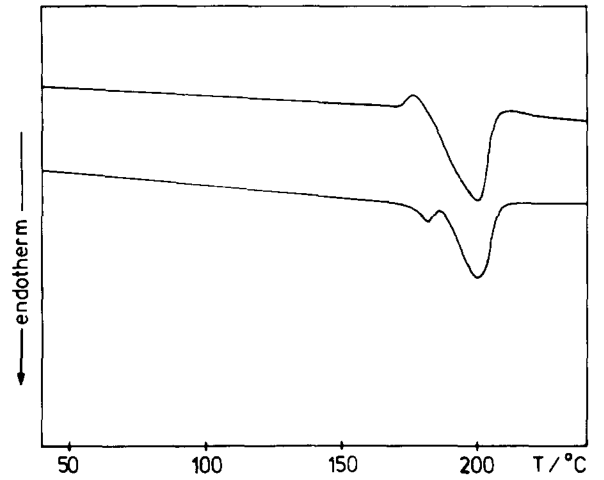


Figure 5 D.s.c. traces of poly(amidourethane)s **32** (lower curve) and **34** (upper curve) at heating rate 20°C min^{-1}

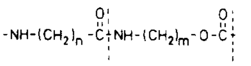
are alternating too and somewhat lower if the latter is a homopolymer (Perlon-6).

EXPERIMENTAL

Reagents and solvents

These were purified and dried before use according to known procedures. Isocyanatoacyl chlorides[10] and *N*,*O*-bis(trimethylsilyl)aminoalcohols[17] were prepared as described in the literature[17]. All reactions were made in flame-dried glass equipment in an argon atmosphere. Synthesis and properties of diisocyanatodicarboxamides and poly(diamidodiurethane)s have been published elsewhere[13].

Table 4 Comparison of melting points of alternating poly(amidourethane)s (PAU) and corresponding polyamides (PA)

	 $-NH-(CH_2)_n-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_m-O-\overset{O}{\overset{\|}{C}}-$		T_m (°C)	
	$n+1$	$m+2$	PAU	PA
31	4	4	190–196	259–262
32	4	6	194–197	195–200
33	6	4	198–204	195–200
34	6	6	199–204	228/250

Methods of characterization

I.r. spectra were recorded on a Beckman Acculab 4 spectrometer as films or nujol mulls between NaCl plates. ^1H n.m.r. spectra were made on a Bruker WP 80 in deuterodimethylsulphoxide or $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Viscosimetry was made with an Ubbelohde-type viscosimeter. The thermal properties were investigated with a Thermal Analyzer

990 with d.s.c. equipment (Du Pont). Heating rates were $20°C\,min^{-1}$.

N-Trimethylsilyloxyalkylisocyanatocarboxamides (**15–20**)

The isocyanatoacyl chloride (50 mmol) was mixed with 100 ml toluene cooled to −5°C, stirred and 50 mmol of an *N,O*-bis(trimethylsilyl)aminoalcohol added so that the temperature of the mixture did not exceed +5°C. When the addition was complete, the mixture was allowed to warm to room temperature and was stirred for 1 h. The volatile compounds were removed under reduced pressure and the remaining crude products were purified by short-path distillation in vacuum. Correct elemental analyses were obtained for all compounds. For properties, b.p., yields, i.r. absorptions and n.m.r. data, see *Table 1*.

Poly(diamidodiurethane)s (**21–30**)

1,4-Butanediol (2.5 mmol) was dissolved in 10 ml dimethylacetamide and a diamidodiisocyanate (2.5 mmol) was added, stirred and heated to 80°C for 12–20 h. The polymers were precipitated in methanol, filtered off and dried *in vacuo*. For m.p., yields, i.r. absorptions and η_{inh}, see *Table 2*.

Poly(amidourethane)s (**31–34**)

Pyridine (10 ml), 0.5 g of 70% HF in pyridine, 5 mmol of an *N*-(trimethylsiloxy)isocyanatocarboxamide and one drop of dibutyltin dilaurate were stirred at 50°C until the isocyanate had reacted (i.r. control), some 8 h. The polymers were filtered off, washed with methanol, dissolved in 5 ml dimethylformamide, precipitated in methanol and dried *in vacuo*. For m.p., yields, i.r. absorptions and η_{inh}, see *Table 3*.

CONCLUSIONS

Diamidodiisocyanates and trimethylsiloxyalkylamidoisocyanates are classes of intermediates or monomers for the synthesis of poly(amidourethane)s with regular sequence of amide and urethane groups, whose properties can be varied in a wide range without losing the regular structure. Extension to fully aromatic diamidodiisocyanates and to other reactions of isocyanates (polyimides, polyureas, etc.) will open up further possibilities.

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REFERENCES

1 Ober, Ch. K., Jin, J. I. and Lenz, R. W. *Adv. Polym. Sci.* 1984, **59**, 103; Percec, V., Schaffer, T. D. and Nava, H. *J. Polym. Sci., Polym. Lett. Edn.* 1984, **22**, 637

2 Kurita, K., Matsuda, S. and Iwakura Y. *Makromol. Chem.* 1981, **182**, 1327

3 Tanaka, M. and Nakaya, T. *Kobunshi Robunshu* 1986, **43**, 311; *Makromol. Chem.* 1986, **187**, 2345; *J. Macromol. Sci.-Chem. (A)* 1987, **24**, 777

4 Mormann, W. and Hissmann, E. *Tetrahedron Lett.* 1987, **28**, 3087

5 Mormann, W. and Leukel, G. *Synthesis* 1988, 990

6 Mormann, W. and Brahm, B. *Makromol. Chem., Rapid Commun.* 1988, **9**, 175

7 Mormann, W. and Brahm, B. unpublished results

8 Mormann, W. and Brahm, M. *Makromol. Chem.* in press

9 Iwakura, Y., Uno, K. and Kang, S. *J. Org. Chem.* 1966, **31**, 142

10 Iwakura, Y., Uno, K. and Kang, S. *J. Org. Chem.* 1965, **30**, 1158 and references therein

11 Bruynes, C. A. and Jurriens, T. K. *J. Org. Chem.* 1982, **47**, 3966

12 Fink, W. *Chem. Ber.* 1964, **97**, 1433

13 Mormann, W. and Hohn, E. *Makromol. Chem.* submitted for publication

14 Kricheldorf, H. R. *Makromol. Chem.* 1973, **167**, 1

15 Ulrich, H., Tucker, B. and Richter, R. *J. Org. Chem.* 1978, **43**, 1544

16 Brandrup, J. and Immergut, E. H. (Eds.) 'Polymer Handbook', Wiley-Interscience, New York, 1975

17 Lukevits, E., Liberts, M. G. and Voronkov, M. G. *Zh. Obshch. Khim.* 1969, **39**, 806

18 Kricheldorf, H. R., Leppert, E. and Schilling, G. *Makromol. Chem.* 1974, **175**, 1705