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Synthesis and Characterization of Polyurethanes With High Content of Biuret Groups

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An ^{1}H-NMR and ^{13}C NMR study of the reaction between urea and 4,4'-diphenylmethanedisocyanate is reported. Assignments for individual signals of biuret groups were determined and their concentration dependence on the reaction time was established. The rate constants for different biuret oligomers were calculated. From biuret oligomers and urethane oligomers block cooligomers and later block copolymers were formed.

INTRODUCTION

The reaction between isocyanates and polyols leads to the formation of urethane bonds, while the reaction between water and isocyanates leads to amines and later to biurets. Urea reacts with isocyanates in a manner similar to amines due to two very reactive difunctional — NH_2 groups. In the first step of the reaction, oligomers of mono- and disubstituted biurets can be formed. The course of reaction and the concentration of individual products depend on the reaction conditions and the molar ratio between urea and isocyanates. Owing to the tetra-functionality of urea and to the difunctionality of isocyanates, the higher molecular products are highly branched and, ultimately, crosslinked.[1]

In the present work some reactive oligomers derived from urea and isocyanates were synthesized and characterized. Then the biuret oligomers derived from urea were allowed to react with urethane oligomers to form highly crosslinked polyurethanes. The compositions of the biuret and urethane oligomers were determined by ^{1}H-NMR, ^{13}C-NMR and GPC, while the crosslinked polyurethanes were characterized by IR spectroscopy.

EXPERIMENTAL

All materials used in this work were products of Merck and Schuchardt. Isocyanates, urea and solvents were purified and dried before use.

The urea-isocyanate oligomers were prepared at room temperature from 3.75 molar solutions of urea in DMF or DMF-d_6 by adding pure phenylisocyanate (PHI) or 4,4'-diphenylmethanediisocyanate (MDI) to the solution. The molar ratios of urea : isocyanate were 1 : 1, 1 : 2 and 2 : 1. The reactions took place for 24 hours. ^{1}H- and ^{13}C-NMR spectra of the reaction mixtures were recorded between one and two hours after the reactions started. The urethane oligomers were prepared from 3.75 molar solutions of PHI or MDI and ethylene glycol (EG) in DMF or DMF-d_6 mixed in molar ratios of 1 : 1, 2 : 1 and 1 : 2 at room temperature. The compositions of the products were determined by ^{13}C-NMR and GPC. The block urethane-biuret cooligomers were formed in some cases from urea oligomers with free-NH_2 groups and urethane oligomers with free-NCO groups and in other cases from urea oligomers with free-NCO groups and urethane oligomers with free-OH groups.

The ^{13}C-NMR spectra were recorded on a Jeol FT 90 Q spectrometer at 22.5 MHz, pulse width 15 μs (90° pulse angle) and spectral width 5000 Hz. For all spectra, chemical shifts were quoted with respect to TMS as standard. All spectra were proton decoupled. The time delay was 5 s.

GPC analyses of urethane oligomers were conducted using 100 and 500 Å μ-Styragel columns and THF as solvent. Assignments for individual signals in the spectra and chromatograms were made: a) on the basis of data from model compounds, which were synthesized from isocyanates and water or from monofunctional isocyanates (PHI) and urea; b) on the basis of data from reference substances;[2–5] and c) on the basis of changes in the concentrations of individual substances which occured during the reactions, by correlating disappearances of signals or species consumed by the reaction. The GPC chromatograms were assigned as was described before.[6]

RESULTS AND DISCUSSION

There are many types of possible reactions between urea and isocyanates. In the first step, isocyanate reacts with an —NH_2 group of urea to form a monosubstituted urea, which later reacts through different mechanisms to

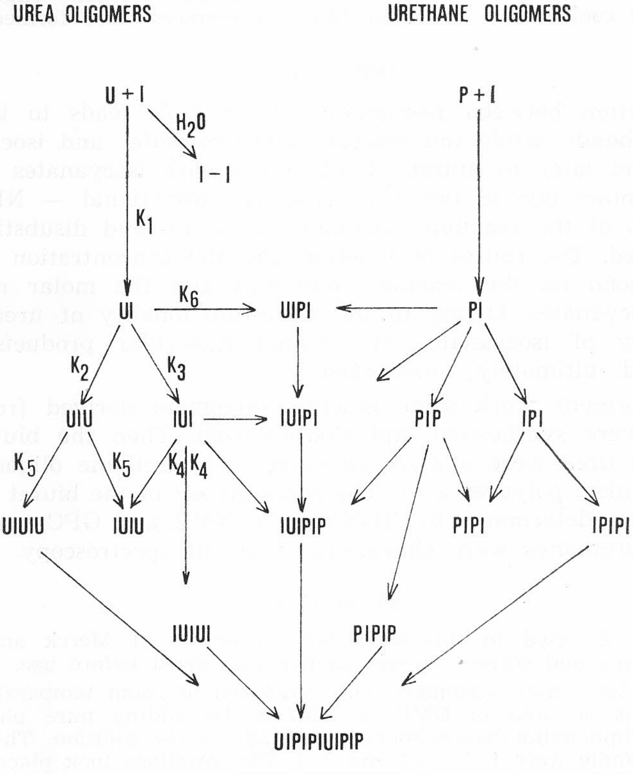


Figure 1. The expected course of reactions between urea (U) and isocyanate (I) or polyol (P) and isocyanate (I) and formation of random urea — isocyanate — polyol terpolymer

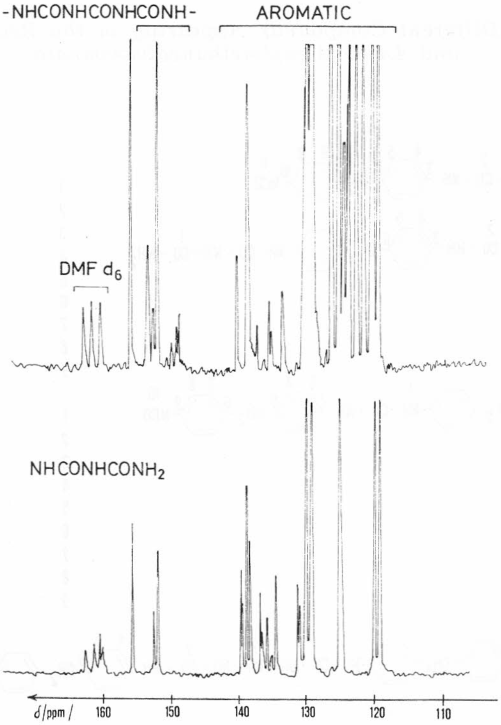


Figure 2. ^{13}C NMR spectra of reaction products derived from urea and phenylisocyanate a) after two hours, b) after 24 hours. Solvent DMF-d_6

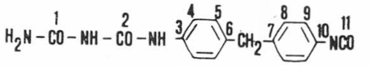
form a disubstituted urea. The formation of tri- and tetrasubstituted urea is also possible, but only in cases when the ratio between urea and isocyanate is 1 : 3 or more. Substituted ureas further react with isocyanate to form biurets, which in higher stages of the reaction are partly crosslinked and partly soluble. Apart from these, other side reactions are also possible. The expected course of the reaction is shown in Figure 1, where I, U and P represente isocyanate, urea and polyol, respectively, and where IU, UIU, IUI *etc.* represent various oligomers. In the ^{13}C-NMR spectra of the reaction products obtained from urea and phenylisocyanate, two prevailing regions can be seen (Figure 2). The region between 119 and 142 ppm is due to aromatic carbons, while the region between 150 and 160 ppm is due to —CO-groups of substituted ureas and biurets. The —CONCONH$_2$ groups of biurets derived from PHI and MDI have two —CO— signals at 153.1 and 156.8 ppm. Formation of higher molecular species shifts the —CO— signals of —NHCOHN-groups to a higher field (150 to 153 ppm). The observed chemical shifts of different carbons in the reaction mixture derived from urea and MDI are given in Table I.

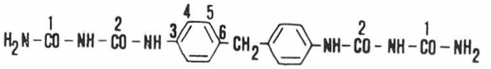
In the proton spectra of the reaction products between urea and MDI, the resonance of —NH— groups occurs between 6 and 10 ppm and that of aromatic protons occurs between 6.9 to 7.8 ppm. Individual signals were

TABLE I

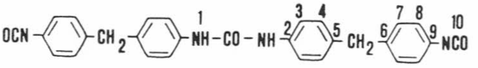
Chemical Shifts of Different Compounds Appearing in the Reaction Between Urea and 4,4'-Diphenylmethanediisocyanate

CARBON - 13

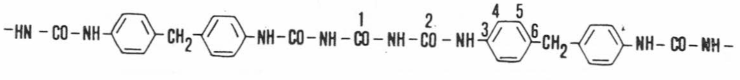




1	156,8
2	153,1
3	120
4	129,7
5	129,7
6	137
7	139,2
8	125,5
9	130,2



1	153,6
2	119,4
3	135,1
4	129,8
5	140,4
6	139,2
7	125,5
8	130,2
9	131,6



1	149 - 150
2	154 - 155
3	122
4	133
5	130
6	140

PROTON

$-\overset{2}{N}H\overset{1}{CONH_2}$

$-NHCO\overset{3}{N}H\overset{4}{CONH}<$

1	5,9
2	10,0 - 10,2
3	9,5 - 10,0
4	8,5 - 9,0

assigned in the same manner as the carbon spectra and the assignments are given in Table I.

In the early stages of the reaction between urea and MDI, the ^{13}C spectra of the reaction mixtures are dominated by —CO— signals of 153.1 and 156.8 ppm, which are due to $CONHCONH_2$ group (UI or UIU). In addition, a signal at 153.6 is noted. This signal is due to substituted ureas, which are formed from MDI and water, which is present in the urea (II). During the course of the reaction, the signals of UI and II oligomers decrease, while new signals between 149 and 155 ppm appear. Separate signals for the UI and UIU oligomers cannot be identified in the ^{13}C and proton spectra of the reaction mixtures. Apparently, isocyanate groups in MDI and —CO—

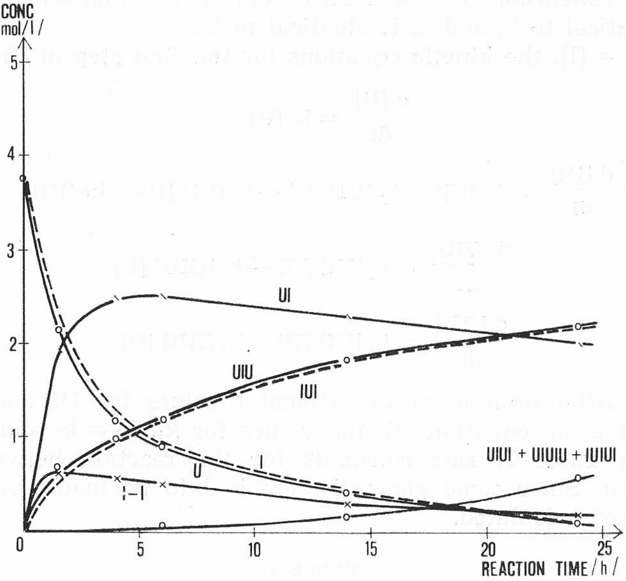


Figure 3. Concentration of compounds appearing during the reaction between 4,4'-diphenylmethanediisocyanate and urea, molar ratio 1 : 1

groups of oligomers UI and UIU are far apart enough not to be effected by one another.

The number of signals observed in the spectra of reaction mixtures agrees very well with the expected course of reaction shown in Figure 1. As the reaction proceeds, the number of signals between 149 and 155 ppm rapidly increases due to the large number of different —CONH-groups generated.

The concentrations of different compounds appearing in the reaction between urea and MDI were determined by measurement of —CONH–-^{13}C NMR signals representing full molecules (Figure 3). For all molar ratios the concentration of UI during the reaction rapidly increases and reaches the maximum in about 5 hours. The concentrations of UIU, IUI and higher oligomers increase in the first step of reaction. For all molar ratios the course of the reactions is similar, but with different concentrations of individual compounds.

Figure 2 shows that oligomers UI and UIU are not separated. In the molar ratio urea : MDI 1 : 1 is

$$[Uo] = [U] + [UI] + [IUI] + 2\,[UIU] + 2\,[UIUI] + \ldots = [Io] \qquad (1)$$

$$[Io] = [I] + [UI] + 2\,[IUI] + [UIU] + 2\,[UIUI] + \ldots \qquad (2)$$

We can conclude, assuming equal reactivity of all species, that

$$[IUI] = [UIU] \qquad (3)$$

and

$$[UI] = ([UI] + [UIU]) + [IUI] \qquad (4)$$

The same conclusions can be drawn from the reaction scheme. This means that k_2 is identical to k_3 and k_4 is identical to k_5.

Since [U] = [I], the kinetic equations for the first step of the reaction are

$$\frac{d\,[\mathrm{U}]}{dt} = k_1\,[\mathrm{U}]^2 \tag{5}$$

$$\frac{d\,[\mathrm{UI}]}{dt} = k_1\,[\mathrm{U}]^2 - k_2\,[\mathrm{UI}]\,[\mathrm{U}] - k_3\,[\mathrm{UI}]\,[\mathrm{U}] - k_6\,[\mathrm{UI}]^2 \tag{6}$$

$$\frac{d\,[\mathrm{UIU}]}{dt} = k_2\,[\mathrm{UI}]\,[\mathrm{U}] - k_5\,[\mathrm{UIU}]\,[\mathrm{U}] \tag{7}$$

$$\frac{d\,[\mathrm{IUI}]}{dt} = k_3\,[\mathrm{UI}]\,[\mathrm{U}] - k_4\,[\mathrm{IUI}]\,[\mathrm{U}] \tag{8}$$

By time differentiation of experimental values for UI and UIU, which are calculated using equation (4), the values for k_1, $k_2 = k_3$ and $k_4 = k_5$ were calculated. In Table II rate constants for the reaction between urea and MDI are given. Since some generalization had to be made, other rate consatnts were not calculated.

TABLE II

Rate Constants for the Reactions of Urea and 4,4'-Diphenylmethanediisocyanate in the Molar Ratio of 1 : 1 ($l\,mol^{-1}\,s^{-1}$)

k_1	$0.48 \cdot 10^{-4}$
k_2	$0.18 \cdot 10^{-4}$
k_4	$0.20 \cdot 10^{-4}$

By comparing the rate constants, we can conclude that the rate of formation of dimers is equivalent to the rate of formation of trimers and tetramers.

The block cooligomers were formed from solutions of biuret oligomers in DMF with free —NH_2 groups and urethane oligomers with free —NCO groups. The compositions of starting samples are given in Table III. Since

TABLE III

Composition of Starting Samples for Formation of Block Cooligomers (mol/l)

Biuret oligomers		Urethane oligomers	
U	0.5	P	0.0
I	0.0	I	0.6
UI	3.4	PI	3.2
UIU	1.9	PIP	0.5
IUI	0.8	IPI	2.1
UIUI + UIUIU	0.9	IPIP + IPIPI	1.1

the resonances of both —NHCOO— urethane groups and —NHCO— biuret groups are between 153 and 155 ppm, most of the signals overlap. Intensities of carbonyl resonances (—NHCONH—) at 156.7 and urethane resonances ($—OCH_2CH_2O—$) at 61.1, 67.1 and 64.7 ppm[7] were used to determine the extent of the reaction. After 4 hours, one-half of the $—CONH_2$ and $—OCH_2CH_2O—$ groups disappeared. Later, the samples became poorly soluble and after one day they were completely insoluble. The average number of units (U or I) in each oligomeric block, which were calculated from the initial composition, was 3.2. The IR spectra show, that after heating the mixture to 150 °C the signals of free-NCO groups completely disappeared and that block copolymers which were insoluble in DMF were formed.

CONCLUSIONS

In the reaction between urea and isocyanates biuret oligomers are formed, which further react with urethane oligomers to form biuret-urethane block copolymers. Using a combination of ^{1}H-NMR, ^{13}C-NMR and GPC it was possible to identify the individual oligomers and to set up a tentative reaction scheme.

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SAŽETAK

Sinteza i karakterizacija poliuretana s visokim sadržajem biuretnih skupina

A. Šebenik

Metodama, ^{1}H NMR i ^{13}C NMR proučavane su reakcije ureje s 4,4'-difenilmetandiizocijanatima. Asignirani su pojedini signali biuretnih skupina i utvrđena je koncentracijska ovisnost vremena reakcije. Izračunane su konstante brzine reakcije za različite biuretne oligomere. Iz biuretnih oligomera i uretanskih oligomera nastaju blok-kooligomeri te zatim blok-kopolimeri.