Chain length regulators in the synthesis of poly(urethane ureas) in solution

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The influence of the type of chain length regulator on the molecular weight, mechanical properties and solution viscosity of poly(urethane ureas) (PUUs) was investigated. As a model, a PUU based on poly(oxytetramethylene)glycol, 4,4'-diphenylmethane diisocyanate, a mixture of ethylenediamine as chain extender and propylene-1,2-diamine as co-chain extender was used. The monoamines diethanolamine (DEA), ethanolamine (EA) and 3(5)-methylpyrazole (3-MP) were compared as chain length regulators. Additionally, model reactions between phenyl isocyanate, n-butylamine and the three monoamines were performed to obtain data about the reactivity and possible side reactions of this mixture. These investigations were carried out by quantitative h.p.l.c. analysis. The lower reactivity of 3-MP led to a minor increase in the molecular weights of the PUUs due to further NCO-conversion, whereas all the mechanical properties of the different polymers were nearly identical. In contrast to 3-MP, however, the application of DEA or EA gave significantly lower solution viscosities, obviously due to the hydroxyl groups of these agents.

(Keywords: poly(urethane ureas); synthesis; chain length regulators; model reactions; h.p.l.c. studies)

INTRODUCTION

Linear polyurethane ureas (PUUs) are common raw materials for highly elastic textile fibres. While the structure, morphology and molecular weight of polymers are decisive for the final properties, the viscosity of the PUU solutions determines their processability. A simple system consisting of a poly(oxytetramethylene)glycol, 4,4'-diphenylmethane diisocyanate and ethylenediamine certainly leads to a good and highly elastic behaviour of the final product. However, it shows insufficient viscosity stability after synthesis, resulting from the formation of a more or less reversible gel[1,2]. This gel formation is due to the very strong hydrogen bonding between the urea groups arising from aliphatic diamines[3–8]. (If aromatic diamines were used as chain extenders, a gel formation was not normally observed, but the properties of the final products were also changed compared with those containing aliphatic amines.)

In order to minimize the interactions in solution, co-chain extender and chain length regulators were added to the PUU components prior to synthesis[9–11]. Aliphatic amines and alkanolamines have been used as typical chain length regulators. Although they are commonly applied, their function has not been clarified completely.

The purpose of this study was to evaluate the effect of the type and concentration of the chain length regulators on solution viscosities and molecular weights. Attendant model reactions of phenyl isocyanate and the chain length regulators were performed in competition to n-butylamine and observed by h.p.l.c. to obtain information about the reaction velocity of the different compounds and the effect of their functionality.

EXPERIMENTAL

Materials

Poly(oxytetramethylene)glycol (Polymeg 2000, QO Chemicals) was dried at 70°C and 1.5×10^{-4} MPa prior to use. 4,4'-Diphenylmethane diisocyanate (MDI; SYStanat MS, BASF Schwarzheide) and phenyl isocyanate (PI; Merck) were used as commercially available (purity > 99.8%). Diamino-1,2-propane (PDA) and ethylenediamine (EDA) were distilled over sodium. n-Butylamine (BA), ethanolamine (EA), diethanolamine (DEA) and 3(5)-methylpyrazole (3-MP) were fractionated four to five times. *N*,*N*-Dimethylformamide (DMF) was stored over a 4 Å molecular sieve for 3 weeks. Acetonitrile (ACN; PCK Schwedt, u.v. spectroscopy grade) was used without further purification.

Polymer synthesis

MDI and Polymeg were mixed at 40°C in a ratio of 1:1.84. Then the mixture was heated to 80°C and kept at this temperature for 2 h to complete the reaction. After cooling to room temperature the obtained prepolymer was dissolved in DMF (concentration 50% w/w). In a stirring vessel EDA and PDA were mixed with the chain length regulators and DMF, and the prepolymer solution was added dropwise at 0–5°C within 45 min. The amount of the diamines was equivalent to the estimated NCO content of the prepolymer and the ratio of EDA:PDA was 7:3. EA, DEA and 3-MP were added in a concentration of 3, 6 and 9 mol% related to the diamines

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in the diamine/DMF mixture. All the reaction steps were performed under dry nitrogen.

Characterization of the PUU

The solution viscosities were measured using a Hoeppler rheoviscosimeter. Mechanical measurements were carried out with a Tiratest 2160 instrument on foils of about 150 μm thickness. The molecular weights were estimated by g.p.c. (Mercko-Gel Si 5000, 1000, 500, 200; eluent DMF; detection r.i.; Waters R 403).

H.p.l.c. studies

Sample preparation. BA, one of the chain length regulators, and DMF were placed in a double-walled glass flask and kept at a temperature of 10°C. For 10 min different amounts of PI were added dropwise to these mixtures, which were then kept at room temperature for 1 h. The possible reaction products are given in *Figure 1*. In the case of excessive NCO, methanol was added after the reaction to form the corresponding *N*-phenyl methylcarbamate, **10**. Side reactions in the presence of water traces afforded the compounds **8**, **9** and **11**. The formation of the products **8–11** is given in *Figure 2*. The model compounds **1–5**, **7** and **9–11** were synthesized by conventional methods and purified by recrystallization and triple fractionation. Their purity was checked by h.p.l.c.

Analytical conditions. The separation was performed by means of a Hewlett Packard HP 1084 A chromatograph and detected by u.v. at 254 nm. Columns: RP-18-404, 5 μm (Central Institute of Organic Chemistry) and 1425 RP for separating **1** from **5**. Mobile phase: H_2O/ACN (gradient mode).

The quantitative evaluation of the chromatograms was realized by using an HP 79850 A integrator. Naphthalene, **12**, was the internal standard. Retention times and response factors of the compounds are given in *Table 1*.

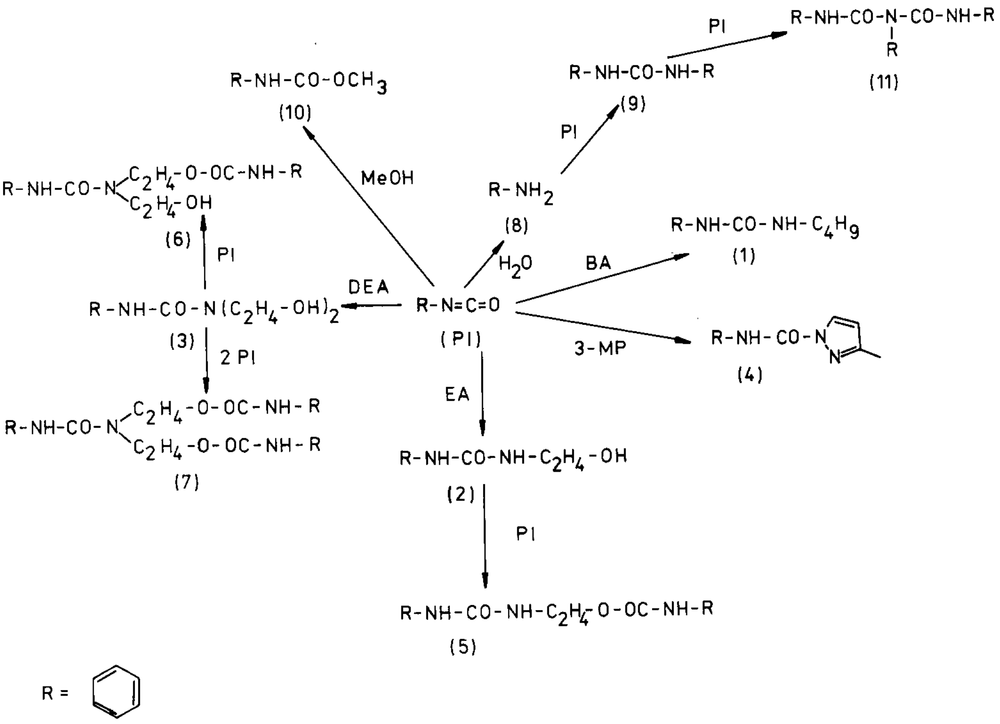

Figure 1 Scheme of the reaction of phenyl isocyanate with nucleophiles

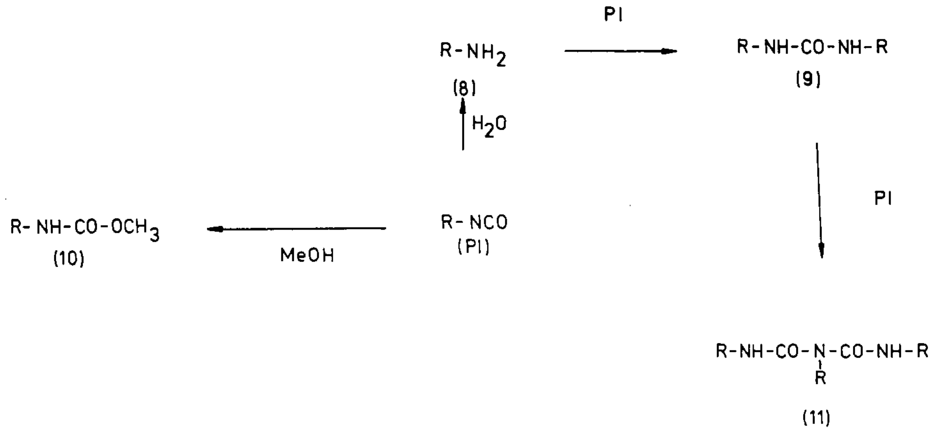

Figure 2 Methanol blocking and water side reactions of the isocyanate group

Table 1 H.p.l.c. data of model compounds

Substance	Code	Number	Retention time (min)	Response factor (amount/area)
Column RP-18-404				
N,*N*-Di(β-hydroxyethyl)-*N'*-phenyl urea	PDEAU	**3**	1.37	7.8216×10^{-7}
N-β-Hydroxyethyl-*N'*-phenyl urea	PEAU	**2**	1.40	1.0049×10^{-6}
Aniline	–	**8**	2.30	2.0341×10^{-6}
N-Phenyl methyl carbamate	PMC	**10**	3.16	4.7707×10^{-6}
N-Butyl-*N'*-phenyl urea	PBU	**1**	4.46	9.8141×10^{-7}
N-β-Phenylcarbaminoethyl-*N'*-phenyl urea	PEAUC	**5**	not separable from 1 on this column	
N,*N'*-Diphenyl urea	DPU	**9**	5.85	1.3534×10^{-7}
N-Phenyl-*N'*-pyrazoyl urea	PMPU	**4**	7.78	2.5316×10^{-7}
Naphthalene	–	**12**	11.76	1.1308×10^{-6}
N,*N'*,*N''*-Triphenylbiuret	TPB	**11**	13.21	2.8587×10^{-7}
Column 1425 RP				
N-β-Hydroxyethyl-*N'*-phenyl urea	PEAU	**2**	1.80	1.0245×10^{-6}
N-Phenyl methyl carbamate	PMC	**10**	2.58	4.6029×10^{-6}
N-Butyl-*N'*-phenyl urea	PBU	**1**	3.75	9.1521×10^{-7}
N-β-Phenylcarbaminoethyl-*N'*-phenyl urea	PEAUC	**5**	5.67	1.4129×10^{-6}

RESULTS AND DISCUSSION

Model reactions

The amines react with the free NCO groups to yield chain-terminated urea derivatives according to *Figure 1*. Unlike 3-MP the alkanolamines can be additionally converted into urethane ureas (**5**–**7**) if there is an excess of free NCO. In this way crosslinking is also possible in the polymer. Traces of water additionally give the corresponding amines and ureas of the isocyanate used (*Figure 2*).

The h.p.l.c. results of the PI reaction with the chain length regulators and the BA have been summarized in *Table 2*. These findings permit the following conclusions.

1. In the molar ratio of 1:1:1 for PI:BA:chain length regulator the BA and the alkanolamines show nearly the same reaction velocity (50% NCO conversion of each substance), whereas only 5% of the corresponding pyrazole urea is formed (series A).
2. This behaviour has also been found at a 10:1 ratio of the primary amine to the chain length regulator. The hydroxyl groups of the alkanolamines do not react with the isocyanate as long as there is any excess of amine groups.
3. Higher levels of isocyanate excess promote the alkanolamine-based urethane urea formation. At least in the case of EA, at a ratio of NCO to the H-active compounds of 1.25:1, about 28% of the NCO excess is converted into the urethane urea **5** (series C).
4. Traces of water also react in the presence of a higher NCO excess, but only when the amines have already been converted almost completely (series C, traces of diphenyl urea).
5. This behaviour is also confirmed by the experiments given in *Table 3*, where the isocyanate–amine reaction in the presence of water is presented. The urea derivative of BA was found in the theoretical amount. Water reacts only with an NCO excess, leading to the aniline side products, **9** and **11** (*Figure 2*). The formation of triphenylbiuret at low temperatures is remarkable in this short time. However, it is in full agreement with earlier results[12].

Solution and mechanical properties of the PUU

The chain length regulators investigated differ in their functionality and basicity. Consequently they must show a variable reaction behaviour towards the NCO group. Hence, different molecular weights with the corresponding viscosities should result. The estimated molecular weights and viscosities of PUU synthesized as DMF solutions of 12.5% are given in *Table 4*.

The higher the content of a chain length regulator, the lower the M_w and M_n values. The PUU samples containing alkanolamines differ remarkably from those including 3-MP. The viscosities of the latter are considerably higher than those with the alkanolamines. The samples blocked by 3-MP show a minor increase in their molecular weights compared to those blocked by alkanolamines. This is probably due to the lower reactivity of the pyrazole and the further NCO-conversion of the polymer, as shown in the previous section. On the other hand, the viscosity behaviour of the solutions seems to depend more on the chemical structure of the blocking agents. In the given system the increasing number of hydroxyl groups in the chain length regulators lowers the viscosity, although the molecular weights increase significantly (cf. samples I and VII, II and V, III and VI, VI and IX in *Table 4*). The viscosity of these samples is apparently more closely related to the end groups than to the molecular weights.

A significant influence of the end group on the mechanical properties of the different polymers cannot be observed, as proved by the values in *Table 5*. These properties depend moderately on the end group concentration only in a series of the same agent. Although we have observed minor variations in the molecular weights of PUUs with different chain length regulators, changes in the mechanical properties have not been found. The various chain length regulators can thus be preferably used as viscosity regulators for a desired solution behaviour in dependence on the given

Table 2 Reactivity of n-butyl amine/chain length regulators mixtures toward phenyl isocyanate (column RP-18-404)

	Initial concentration (mmol) of					Products (mmol)							
Attempt	PI	BA	3-MP	DEA	EA	PBU **1**	PMPU **4**	PDEAU **3**	PEAU **2**	DPU **9**	PMC **10**	PEAUC **5**	NCO conversion (mmol)
A 1	2.5	2.5	2.5	–	–	2.38	0.124	–	–	–	–	–	2.50
A 2	2.5	2.5	–	2.5	–	1.28	–	1.21	–	–	–	–	2.49
A 3	2.5	2.5	–	–	2.5	1.25	–	–	1.18	–	–	–	2.43
B 1	5.0	5.0	0.5	–	–	4.89	0.087	–	–	–	–	–	4.98
B 2	5.0	5.0	–	0.5	–	4.62	–	0.41	–	–	–	–	5.03
B 3	5.0	5.0	–	–	0.5	4.46	–	–	0.38	0.01	–	–	4.86
C 1	6.25	2.5	–	2.5	–	2.98	–	2.35	–	0.047	0.69	–	6.11
C 2	6.25	2.5	–	–	2.5	2.96	–	–	2.47	0.038	0.73	–	6.24
C 3[a]	6.25	2.5	–	–	2.5	2.60	–	–	2.30	0.045	0.75	0.35	6.44

[a] Separation on column 1425 RP

Table 3 The phenyl isocyanate reaction in the presence of water

	Initial concentration (mmol) of			Products (mmol)				
Attempt	PI	BA	H_2O	PBU **1**	DPU **9**	Aniline **8**	TPB **11**	NCO conversion (mmol)
D 1	2.5	2.5	2.5	2.41	–	–	–	2.41
D 2	1.25	2.5	2.5	1.27	0.011	–	–	1.29
D 3	3.75	2.5	2.5	2.41	0.342	0.466	0.0230	3.63
D 4	7.5	2.5	2.5	2.41	2.012	0.9396	0.0302	7.46

Table 4 Dependence of solution viscosities on the type and the concentration of chain length regulators. $c_{PUU} = 12.5\%$ (w/w); solvent DMF; chain extender EDA:PDA = 7:3

Sample	Conversion of prepolymer (%)	Chain controller (mol%)			Viscosity (Pa s) at 30°C		Molecular weight ($g\,mol^{-1}$)		
		EA	DEA	3-MP	1 day	7 days	M_w	M_n	M_w/M_n
I	101.9	9	–	–	3.3	3.5	372 000	183 000	2.0
II	99.9	6	–	–	16.1	17.4	325 000	251 000	1.3
III	99.8	3	–	–	37.9	40.2	543 000	323 000	1.7
IV	101.9	–	9	–	1.2	1.3	226 000	130 000	1.7
V	99.9	–	6	–	10.3	10.3	462 000	271 000	1.7
VI	99.8	–	3	–	31.2	33.5	671 000	417 000	1.6
VII	100.6	–	–	9	12.9	16.1	332 000	234 000	1.4
VIII	100.6	–	–	6	25.0	37.9	561 000	362 000	1.6
IX	100.6	–	–	3	78.1	89.3	604 000	420 000	1.5

Table 5 Dependence of mechanical properties of PUU on the chain length regulators

Sample	Chain length regulator		Viscosity (Pa s) at 30°C, $C_{PUU} = 12.5\%$	Tensile strength		Elongation at break		Permanent elongation (after 300%) (%)
	Substance	(mol%)		(MPa)	confidence interval (%)	(%)	confidence interval (%)	
I	EA	9	3.3	41.5	9.7	905	20.6	9
II	EA	6	16.1	43.0	14.1	1009	20.1	6
III	EA	3	38.0	44.4	10.6	1053	7.4	7
IV	DEA	9	1.2	39.5	16.2	891	28.6	8
V	DEA	6	10.3	41.2	12.5	962	18.5	7
VI	DEA	3	31.2	43.4	11.3	919	15.6	8
VII	3-MP	9	12.9	45.5	10.1	866	11.6	6
VIII	3-MP	6	25.9	44.6	7.7	833	10.9	5
IX	3-MP	3	78.1	43.5	14.9	925	13.8	6

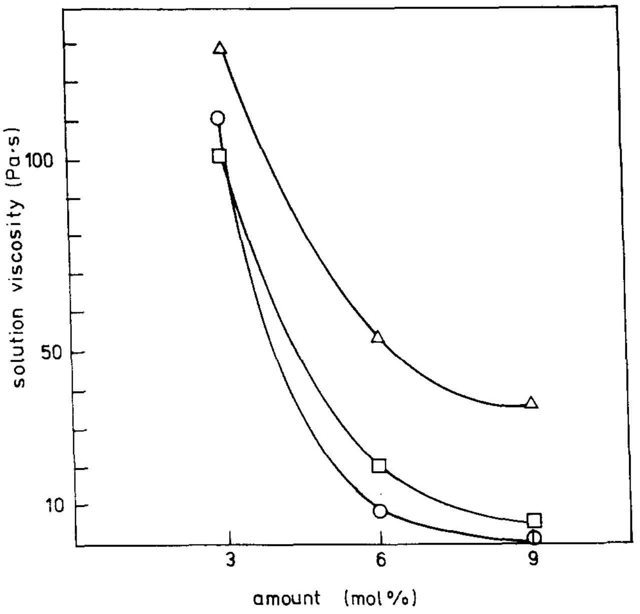

Figure 3 Dependence of the viscosity of a PUU solution in DMF (c_{PUU} = 15% w/w) at 25°C on the amount of chain length regulators: △, 3-MP; ○, DEA; □, EA

technological regime. Hence, a loss in properties of the final products can be avoided.

CONCLUSIONS

The chain length regulators investigated differ in their reaction velocity. Subsequently, the PUUs show moderately higher molecular weights if 3-MP is used. This behaviour is particularly apparent if higher concentrations (e.g. 9 mol%) of the three chain length regulators are compared. However, these slight differences are not the main reason for the viscosity distinctions observed. The most important aspect is the decrease in viscosity at an increasing content of OH groups in the chain length regulator. We assume that these end groups disturb the interaction between the urea hard segments in the PUU solution. The level of viscosity in dependence on the amount of the chain length regulator can be controlled by the number and the type of functional groups in it. The resulting viscosity vs. chain length regulator curves have different slopes, as shown for EA, DEA and 3-MP in *Figure 3*.

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