Polyurethanes Containing Poly(oxyethylene) Block Units and Their Properties as Polychelatogenes

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SUMMARY:
   Polyurethanes **6** and **7** based on poly(oxyethylene) (**5**) were synthesized and investigated for the application as macromolecular chelating agents. 4,4′-Diaminobenzil (**3c**) and 4,4′-diamino-benzil monoxime (**4a**) were prepared as monomer precursors in 70 and 80% yield. Copolymers were obtained in yields between 40 and 60% by polyaddition of the corresponding diisocyanates **3d** and **4b** to poly(oxyethylene) (**5**) of different chain length and characterized by IR and ^{13}C NMR spectroscopy. The application of the resulting polyurethanes containing functional aromatic block units as polychelatogenes was studied in homogeneous phase by membrane filtration. The metal content was determined in both the filtrate and the retentate and in the case of Ni^{2+} at different pH values. At pH 2, for example, the molar binding capacity of a poly-urethane sample of **6** was 3 times as high as that of **5**.

Introduction

Polychelatogenes for the enrichment and removal of metal ions from diluted solutions have found considerable interest[1–4], whereas crosslinked, insoluble resins implicate substantial disadvantages, e.g. long contact time for the absorption equilibrium. Soluble chelating agents overcome these difficulties by reaction in homogeneous phase.

Recently, we have investigated a number of macromolecular chelating agents in terms of their preparation and potential technical application[1,5–7]. These poly-chelatogenes have been synthesized by copolymerization or polymer-analogous reactions and have been successfully applied to the removal of various metal ions from diluted solutions. Most of these polychelatogenes contained relatively strong chelating groups like nitrogen and sulfur ligands, and carboxylic groups.

This paper reports on the synthesis of polyurethanes based on poly(oxyethylene) with weak chelating units such as benzil groups. The pH dependancy of the metal uptake capacity as well as the influence of the block units of poly(oxyethylene) in the polyurethanes are investigated and discussed. Since poly(oxyethylene) itself has a certain metal binding capacity, we were interested in which way the metal binding is changed by insertion of diketone and α-ketoxime moieties into the chain.
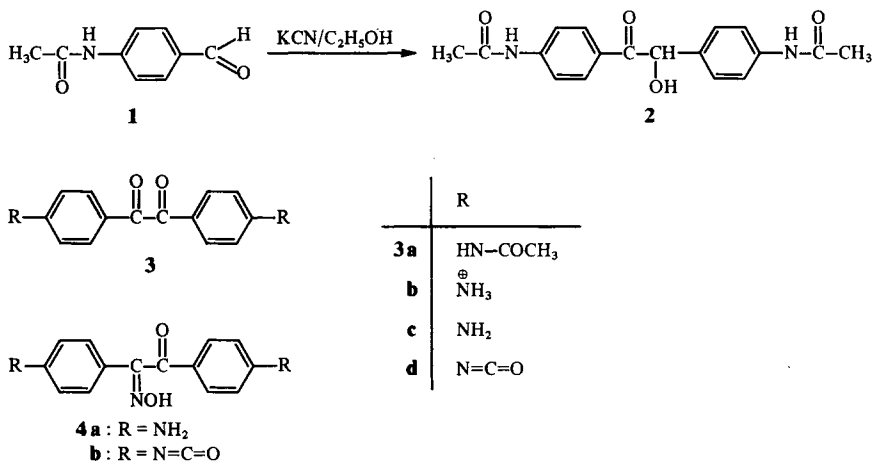
Results and Discussion

As chelating units we introduced 4,4′-diaminobenzil (**3c**) and 4,4′-diaminobenzil monoxime (**4a**) which, after conversion of the amino groups into isocyanate groups,

were reacted with bifunctional oligomers and polymers, e. g. poly(oxyethylene). The results were expected to be a basis for the assessment of the influence on the complex forming capacity of poly(oxyethylene) which is able to bind metal ions itself[8, 9].

Polyamides containing poly(oxyethylene) were described by Kern et al. [10] and polyamides with aromatic units have been reported by Santappa et al. [11]. However, syntheses of polyurethanes with poly(oxyethylene) block units and benzil groups have not yet been mentioned in the literature.
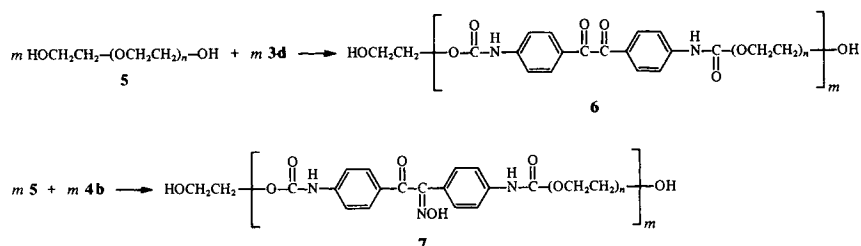
Synthesis of monomers

Starting from *p*-aminobenzaldehyde, 4,4-diaminobenzil (3c)[12] was obtained in four reaction steps via 2, 3a, and 3b (see Exptl. Part). As attempts to obtain the isocyanate 3d by reaction with phosgene failed, *N,N'*-carbonyldiimidazole in tetrahydrofurane was used successfully for the conversion of 3c into 3d. In addition, this method avoids working with the toxic phosgene and allows a handy reaction procedure. In the same way 4b was prepared from the monoxime 4a which was obtained following a general procedure[13].

$$H_3C-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\text{(C}_6\text{H}_4\text{)}-\underset{H}{C}\overset{H}{\underset{O}{\diagup}} \quad \xrightarrow{\text{KCN/C}_2\text{H}_5\text{OH}} \quad H_3C-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\text{(C}_6\text{H}_4\text{)}-\underset{O}{\overset{O}{\parallel}}C-\underset{\underset{OH}{|}}{CH}-\text{(C}_6\text{H}_4\text{)}-\underset{H}{N}-\underset{\underset{O}{\parallel}}{C}-CH_3$$

	R
3a	HN—COCH₃
b	$\overset{\oplus}{NH_3}$
c	NH₂
d	N=C=O

4a : R = NH₂
  b : R = N=C=O

Oligomer and polymer synthesis

By reaction of compounds 3d and 4b with α-(2-hydroxyethyl)-ω-(hydroxy)poly-(oxyethylene) (5) polyurethanes 6 and 7 were obtained. By variation of the chain length of 5 the number of functional groups per chain as well as the molecular mass and composition of the block copolymers can be regulated.

The reaction was carried out in toluene in a 1:1 mole ratio by addition of the diisocyanate to the polymeric glycol 5. Monitoring the reaction by IR spectroscopy showed a decrease of the isocyanate band (2260 cm⁻¹) and an increase of the urethane band (1710 cm⁻¹).

$m\ HOCH_2CH_2-(OCH_2CH_2)_n-OH\ +\ m\ \mathbf{3d}\ \longrightarrow$ ... reaction scheme **6**

$m\ \mathbf{5}\ +\ m\ \mathbf{4b}\ \longrightarrow$ ... reaction scheme **7**

The polymers were precipitated in diethyl ether and after isolation fractionated by membrane filtration in water. The resulting products show a good solubility in water as well as in a series of organic solvents.

Chelating properties of the polymers

For comparison the chelating properties of **5** were investigated (Fig. 1). The ability of forming metal chelates was found to be relatively low considering the amount of available ether oxygen as donating group. Even if one assumes that four oxygen atoms bind one metal ion like an open crown ether, less than 1% of the oxygen atoms participate in the chelate formation. It is obvious that this cannot be attributed to conformational aspects of the polymer. The small amount of metal chelates formed must be due to the fact that water molecules and ether oxygen are not very different with respect to the stability of their complexes. Therefore, complicated equilibria between the polymer complexes, mixed polymer-aquo complexes and aquo complexes exist, whereas under the conditions chosen the formation of aquo complexes is dominant.
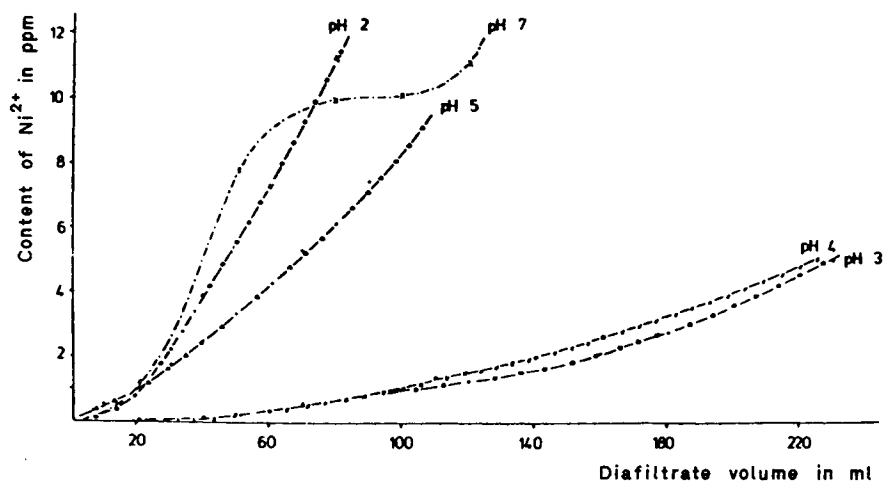

Fig. 1. Chelating curves of poly(oxyethylene) (**5**) ($M = 12\,000\ g \cdot mol^{-1}$) with Ni^{2+} ions at different pH values

Figs. 2 – 5 show the chelating curves for 3 samples of polyurethane **6** containing benzil groups with nickel ions at different pH values. If the benzil group would be a stronger chelating group than the ether oxygen an increase in metal binding would be expected with increasing amounts of benzil groups in polymer **6** from sample C to A (Tab. 1).

Tab. 1.   Binding capacities of the polyurethanes for Ni^{2+} ions

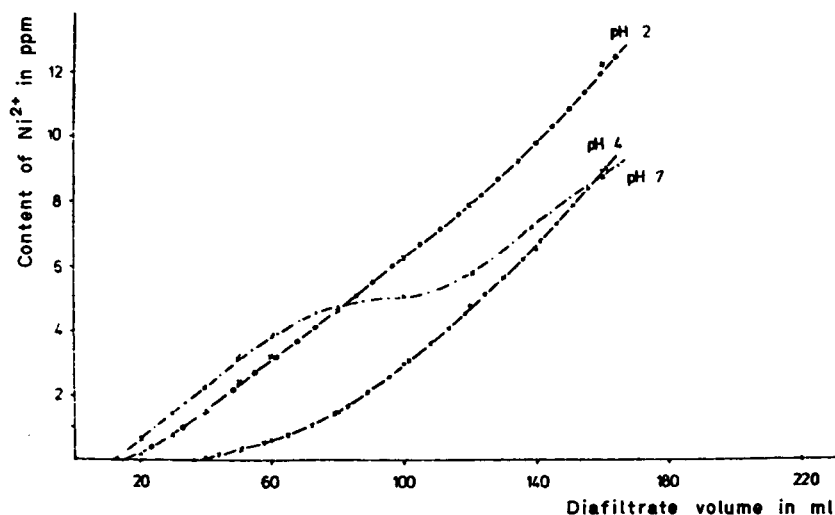| Polymer	Sample	n	Metal capacity in mg metal/g polymer (mmol/g polymer)		
			pH 2	pH 4	pH 7
5	A [a]		4 (0,07)	36 (0,61)	16 (0,27)
6	A	7	10 (0,17)	12 (0,20)	23 (0,39)
	B	23	7 (0,12)	8 (0,14)	39 (0,66)
	C	46	15 (0,25)	9 (0,15)	19 (0,32)
7	A	23	10 (0,17)	29 (0,49)	19 (0,32)

[a] $n = 273$.

Fig. 2.   Chelating curves of polyurethane **6** sample A (Tab. 1) with nickel ions at different pH values

The values given in Tab. 1 do not confirm this. Again, only a small percentage of the available chelating groups binds nickel ions. Sample A of polymer **7** with benzil monoxime units shows a behaviour for binding of nickel similar to **5** sample A. These
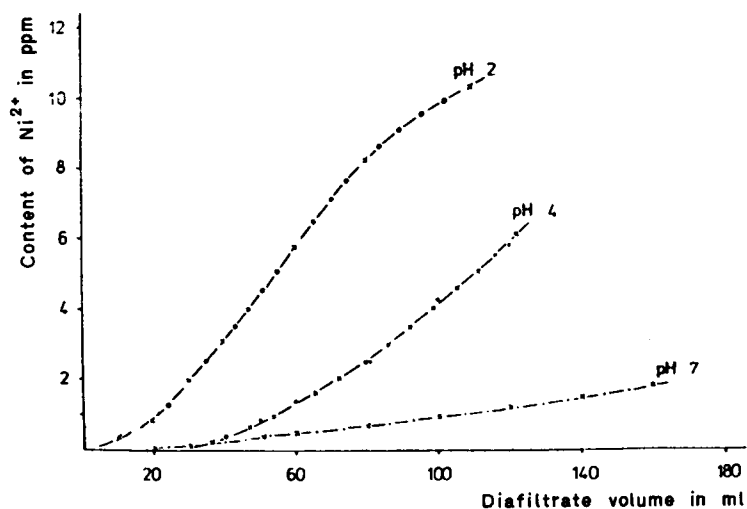
Fig. 3. Chelating curves of polyurethane 6 sample B (Tab. 1) with nickel ions at different pH values
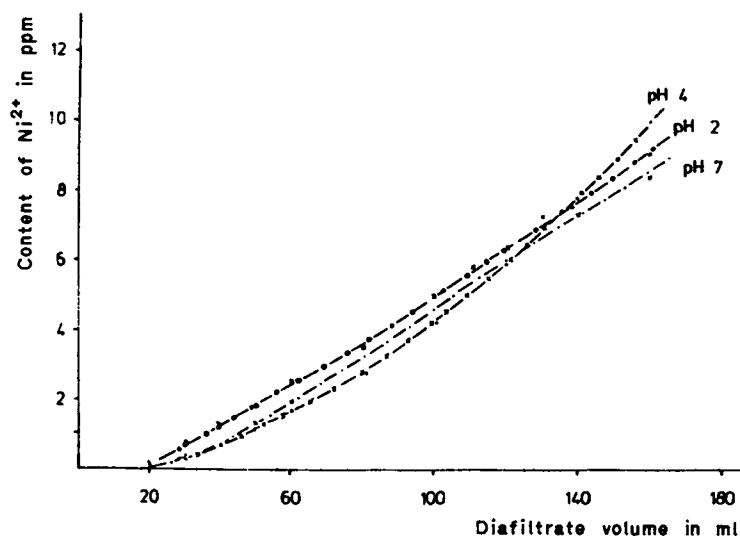

Fig. 4. Chelating curves of polyurethanes 6 sample C (Tab. 1) with nickel ions at different pH values

results clearly indicate that under the conditions chosen in aqueous solution ether, benzil, and benzil monoxime groups are comparable in their metal binding properties.
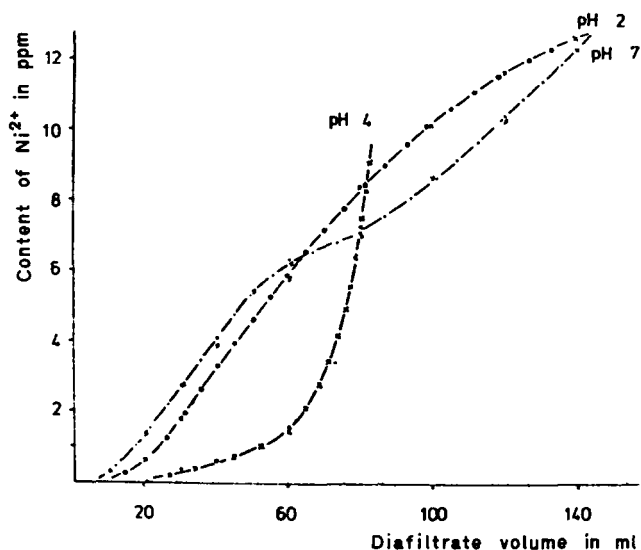
Fig. 5. Chelating curves of polymer 7 sample A with nickel ions at different pH values

Furthermore, in all cases only a small amount of the polymer-bound chelating groups participate in metal binding because water competes with the chelating sites of the polymer. Considering this and the complicated equilibria of various chelate species it is obvious that the metal capacity depends on many factors like ligand exchange reactions and their kinetics, e.g. on the flow rate of water through the membrane filtration cell. Additionally, the accuracy of the method of determination of the metal capacity is limited due to the low slope of the curves[5]. Therefore, the differences observed in metal binding of polymers cannot be attributed only to the thermodynamic stability of one complex species or to their differences.

The metal binding capacity of these polymers is too low for practical use. Nevertheless, the binding curves (Figs. 2 – 5) indicate the complicated ligand exchange reactions which are strongly dependant on pH. So far, it is not possible to derive from these data any molecular view of the species participating in those equilibria.

Experimental Part

For spectroscopic studies the following instruments were used: IR spectra with "Infracord" (Perkin Elmer), NMR spectra with "NMR-Spectrometer Bruker WP 60" and "NMR-Spectrometer Bruker WH 90 with computing unit BNC 28". Determination of the metal content was carried out with the "Atomic absorption spectrometer 1248" (Beckman) and the elemental analyses with the "Elemental Analyser Model 240" (Perkin Elmer). For lyophilization the "Continous Freeze Dryer" (New Brunswick Scientific Co.) was used and for determination of the melting point the "Monoskop IV (Dr. Tottoli)" (Büchi).

Chemicals were purchased from Fluka and Merck and for thin layer chromatography silica gel plates 60 F_{254} (Merck) were used. R_F-values are referred to following solvent mixture: 1-butanol/acetic acid/water (vol. ratio 3 : 1 : 1).

Membrane filtration was carried out with units "Type 401 S" and "Type 420" (Amicon, Holland) and reservoirs as well as with corresponding models of plexiglass which were manufactured in the workshop of our institute. A multifunctional regulator "MFZ", a concentration dialysis selector "CDS 10" and comparable phase selectors were needed for control. Pressure: 250 Pa. "UM2" and "UM10" (Amicon) and comparable filters (Berghof, Tübingen) served as membrane filters[14]. The hydroxyl number of poly(oxyethylene) was determined by UV-spectroscopy[15].

Synthesis of monomers: 4-Aminobenzaldehyde, 4'-formylacetanilide (1) and 4,4'-bis(acetylamino)benzoine (2) were prepared according to literature procedures[12]. 2: yield: 8,0 g (27%) (Lit.[9]: yield 28%); R_F: 0,58; m. p. 240 °C (Lit.[12]: m. p. 244 °C).

All compounds described in monomer synthesis were characterized by elemental analysis, IR spectroscopy and ^{13}C NMR-spectroscopy.

4,4'-Bis(acetylamino)benzil (3a): A mixture of 20 g of copper sulfate, 40 ml of pyridine, and 12 ml of water was heated until a clear solution was obtained. Then, 8 g (25 mmol) of 2 were added in small portions resulting in a change of colour from dark-blue to dark-green. After heating 3 h at 100 °C the reaction mixture was poured into 1 l of water at room temperature. The precipitate was filtered off and washed with water. After recrystallization from diluted acetic acid (50 wt.-%) the compound was dried over P_4O_{10} in a high vacuum. Yield: 5,4 g (68%); m. p. 242 – 243 °C.

^{13}C NMR (DMSO, Stand.: DMSO, $\delta = 39,5$): $\delta = 193,71$ (CO—CO); 169,36 (CO—CH$_3$); 145,56, 131,05, 127,05, 118,79 (C$_6$H$_6$); 24,14 (CH$_3$).

4,4'-Diaminobenzil (3c): 4,0 g (12 mmol) 4,4'-bis(acetylamino) benzil 3a were heated in a mixture of 50 ml of methanol and 15 ml of conc. hydrochloric acid until a yellow precipitate was formed. After cooling and filtration of the product it was dissolved in 50 ml of water and then aqueous ammonia was added in order to precipitate the compound. After recrystallization from ethanol thin layer chromatography showed that the compound is pure. Yield: 2,0 g (69%); m. p. 169 °C. R_F: 0,63.

^{13}C NMR (DMSO, Stand.: DMSO, $\delta = 39,5$): $\delta = 193,62$ (CO); 155,98, 132,25, 119,96, 113,03 (C$_6$H$_6$).

4,4'-Diaminobenzil monoxime (4a): A mixture of 3c (2 g; 8 mmol), hydroxylamine hydrochloride (2,3 g), barium carbonate (2,4 g), and 50 ml of ethanol was refluxed for 5 h. The hot solution was filtered and the precipitate isolated by filtering off after cooling. After recrystallization from ethanol the product was dried over P_4O_{10} in a high vacuum. Yield: 1,6 g (80%). R_F: 0,67; m. p. 186 – 187 °C.

^{13}C NMR (DMSO, Stand.: DMSO, $\delta = 39,5$): $\delta = 192,49$ (CO); 155,88 (CNOH); 154,67, 131,60, 119,76, 112,90 (C$_6$H$_6$; CO); 150,24, 126,99, 122,98, 113,63 (C$_6$H$_6$, CNOH).

Synthesis of the polymers

Polyurethanes 6 and 7: To a solution of N,N'-carbonyldiimidazole (1,6 g; 10 mmol) in 50 ml of anhydrous tetrahydrofuran, 4,4'-diaminobenzil 3c (1,0 g; 4 mmol) or the monoxim 4a, respectively, in 50 ml of tetrahydrofuran was added dropwise with stirring at 0 °C. After stirring for 1 h and then 2 h at room temperature the volume was reduced to 20 ml by evaporation of the solvent i. vac This solution as well as dibutylbilauroyloxytin (0,3 ml) were added with stirring to a separately prepared mixture of poly(oxyethylene) 5 and 10 ml of anhydrous toluene at 80 °C. After 30 min 10 ml of toluene were added and the reaction mixture was stirred for 2 h at the same temperature. Then, the solvent was removed i. vac the residue taken up in water and extracted twice with diethyl ether in order to remove the tin compound. The aqueous solution was diluted with water to 1 l and fractionated by membrane filtration as described previously[1, 6, 14] (Diaflo UM10 and UM2). The yellow product 6 or 7 was obtained by lyophilization of the retendate. Yields are summarized in Tab. 2. 6 (sample A, $n = 7$): IR (KBr): 3 400 (s; N—H), 1 745, 1 725 (s; C—O), 1 600 (m; C—C arom.), 950 cm^{-1} (m; CH$_2$).

Tab. 2. Experimental data of polymer synthesis

	6 [a]			7 [a] sample A
	sample A	sample B	sample C	
Employed weight of 5 in g (in mmol)	3,0 (10)	2,0 (2)	4,0 (2)	2,0 (2)
Total yield in g (in %)	3,1 (52)	1,5 (60)	2,6 (56)	1,0 (40)
Yield: $\bar{M} > 10^4$ in g (in %)	2,0 (34)	1,0 (40)	2,6 (56)	0,6 (24)
Yield: $2 \cdot 10^4 > M > 2 \cdot 10^3$ in g (in %)	1,1 (18)	0,5 (20)	—	0,4 (16)

[a] See Tab. 1.

^{13}C NMR (D$_2$O): δ = 193,47 (CO—CO); 162,48 (CO—NH); 146,91, 132,82, 128,16, 122,44 (C$_6$H$_6$); 68,74 (CH$_2$—O); 66,63 (CH$_2$).

Metal uptake of the polymers: For the determination of the complex binding capacity the polymer (100 mg) was dissolved in water (200 ml) and adjusted to the corresponding pH by addition of diluted nitric acid or aqueous ammonia. This solution was placed into the membrane filtration cell and the reservoir of the membrane filtration system contained the metal salt solution (50 ppm Ni^{2+}) which has been adjusted to the same pH previously. After completion of the metal uptake the system was washed out until no more metal ions in the membrane filtrate could be detected. Then, the metal concentration of the rentendate was determined by atomic absorption spectroscopy and the polymer was lyophilized for further analytical control.

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