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Polymer 44 (2003) 5075–5101
polymer
www.elsevier.com/locate/polymer

Urethane oligomers as raw materials and intermediates for polyurethane elastomers. Methods for synthesis, structural studies and analysis of chemical composition

Piotr Król*, Barbara Pilch-Pitera

Department of Polymer Science, Faculty of Chemistry, Rzeszów University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

Received 21 January 2003; received in revised form 2 May 2003; accepted 15 May 2003

Abstract

Based on earlier models developed for polyaddition of diisocyanates and polyols, a non-stoichiometric process was provided for step-by-step polymerisation of 2,4- and 2,6-tolylene diisocyanate (TDI) with diols which had various molecule sizes and the nature of polyethers and polyesters. Said process yielded urethane oligomers which had –NCO or –OH groups as their chain end groups. After elimination of excess monomer, these compounds were—at subsequent stages (2–5)—subjected to further reaction with diisocyanate or with selected polyol. The process was operated in bulk and excess monomers were eliminated with the use of the selective extraction method. Linear products were obtained in that way which had well defined chain structures and narrow distribution of their molecular weights (MWD) PD $= \bar{M}_w/\bar{M}_n = 1.1-1.3$. On the basis of IR and mass spectrometry (MS) (electrospray ionization (ESI) and matrix-assisted laser desorption ionization-time of flight (MALDI-TOF)) structural analyses, the expected structures of oligomers were confirmed and the actual compositions of polyurethane mixtures formed at every stage of the polymerisation process could be verified against the data obtained from the model, from the balance calculations (based on determinations of free isocyanate groups) and from the findings of the gel-permeation chromatography (GPC) analysis. Applicability of the presented method was demonstrated and the general scheme was suggested for the process discussed.

Keywords: Polyurethanes; Urethane oligomers

1. Introduction

Some special applications of polyurethanes (PUs), like membranes, coatings which are biocompatible with living tissues and body fluids (e.g. blood) [1,2], liquid crystal mesogenes with non-linear optical properties [3,4], coatings which are modified by covering them with orderly organic mono- and multi-layers [5], and/or waterborne emulsions and dispersions which incorporate polyacrylates and which have the structures similar to those of interpenetrating polymer networks (IPNs) [6,7], require more and more frequently a precisely defined chemical composition and a narrow distribution of molecular weights, both for intermediates and for polyurethanes to be employed in the manufacturing processes. An interesting example for such an application is the synthesis of urethane–vinyl copolymers by the controlled/living radical polymerisation (CRP) method with the use of urethane macro-initiators [8].

It is a relatively difficult task to manufacture products with controlled chemical compositions and narrow MWDs in case of polymers obtained from the step-by-step polymerisation methods. That effect becomes available in chain growth polymerisation processes when the living ion polymerisation method or one of CRP methods (NMP or ATRP) is employed [9]. The progress in step-by-step polymerisation, which is based on the reaction of functional groups in monomers and on converting said monomers into bigger and bigger oligomers and polymers, can be controlled only to some extent by means of the initial molar ratio of functional groups. It is known on the grounds of Flory's theory that the equimolar ratio of functional groups is favourable for the formation of high-molecular-weight polyaddition products, while the polymer so produced will have a considerably high polydispersity PD $= \bar{M}_w/\bar{M}_n \gg 3.0$ at the same time [10]. Our earlier reports demonstrated that the ratio PD could be

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* Corresponding author. Tel.: +48-17-865-1579; fax: +48-17-854-3655. *E-mail address:* pkrol@prz.rzeszow.pl (P. Król).

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doi:10.1016/S0032-3861(03)00431-2

reduced by running a non-stoichiometric polyaddition reaction of diisocyanurate and polyol with considerable excess of one of monomers. However, unconverted excess of that raw material needs to be separated (eliminated) after every process stage. Yet, the formal polymerisation degree DP of the polymer formed at every stage does not exceed 3 then [11,12]. The question arises if that method could be employed to produce linear PUs with well-defined and repeatable chemical structures, and what impact can be expected from that structure on the arrangements of chains within the supermolecular structures, i.e. segments responsible for the flexible and rigid phases of that polyurethane? The generated phase structure is known to be decisive for the physical–mechanical properties of PU plastics. At the early stage, we tried to find the answer to the above question by synthesizing oligourethanes with various molecular weights in the reaction of 2,4-TDI and 2,6-TDI with 1,4-butanediol (BD). The reactions were proceeding in tetrahydrofuran (THF); the solvent was used to control viscosity of the system [11]. Our another study covered numerous stages of the synthesis which was carried out in bulk only and which employed—in addition to BD—also poly(oxyethylene)glycols (POGs) with $\bar{M}_n = 200, 400, 600$ and 1000 g/mol [12].

Having in mind that the supermolecular structures of linear oligourethanes are influenced by the presence of intermolecular hydrogen bonds which are much more numerous in the segments formed with the participation of polyesters than in polyether–urethane segments, it seemed justifiable not only using POGs but also polyester–polyols [13,14]. We decided to utilise polycaprolactone diols (PCDs) with $\bar{M}_n = 530$ and 1250 g/mol.

This report presents the findings from our investigations. Theoretical grounds have been provided for the polyaddition method adopted in the study, the developed ways of producing urethane oligomers with precisely defined compositions and structures have been described, and the findings from structural analyses have been shown.

2. Concept for the step-by-step polyaddition process

The model of the stipulated step-by-step polyaddition process was based on the controlled synthesis procedure that made use of the kinetic model developed for a series of successive-parallel reactions. The scheme was just an expansion of a generally known equation describing the process which yields linear PUs:

$$n\mathrm{HO{-}R_1{-}OH} + n\mathrm{OCN{-}R_2{-}NCO} \longrightarrow \sim(\mathrm{-O{-}R_1{-}O{-}OC{-}NH{-}R_2{-}NH{-}CO-})_n\sim \qquad (1)$$

where R_1 is the aliphatic or aromatic moiety derived from low-molecular-weight diol, polyether–diol or polyester–diol and R_2 is the aliphatic, aromatic or alicyclic moiety in diisocyanate.

The process considered can be presented as a train of successive-parallel irreversible reactions:

$$\mathrm{A} + 4\mathrm{B} \longrightarrow \mathrm{A_1B_2} + 2\mathrm{B}, \qquad \mathrm{A_1B_2} + 4\mathrm{A} \longrightarrow \mathrm{A_3B_2} + 2\mathrm{A}, \qquad \mathrm{A_3B_2} + 4\mathrm{B} \longrightarrow \mathrm{A_3B_4} + 2\mathrm{B}\ldots \qquad (2)$$

wherein each reaction has its specific rate constant k_i. In this scheme: A stands for BD, POG or PCD; B is one of TDI isomers; A_nB_m, the corresponding oligourethane which can be urethane diol $A_{n+1}B_n$ or urethane–diisocyanate A_nB_{n+1}. Oligourethane, which is a product of one or a series of a few reactions, makes a substrate for some subsequent stage and reacts with a monomer, A or B, then.

In the beginning, we utilised kinetic models that were developed earlier, for numerical simulations of the planned processes; the use of different diisocyanates and polyols was assumed [15–17]. The simulation procedures made it possible to calculate changes in concentrations of reacting substances during the process as well as the number-average molecular weight of PUs in relation to the reaction conditions adopted, i.e. molar ratio of functional groups, molecular weight of polyol, and temperature, which was represented with the rate constant k_1 for reaction 1 in scheme (2) utilised in calculations. The developed procedures made it also possible to adjust for changing reactivity of diisocyanate. The so-called substitution effect could thus be considered which is responsible for declining reactivity of the second –NCO group in an aromatic diisocyanate, e.g. in 2,6-TDI, after its first group has been converted into a corresponding carbamate structure [17].

Fig. 1 shows the examples of calculated molecular weights for oligourethanes at successive stages of equimolar ($r = 1$) polyaddition of 2,4-TDI and 2,6-TDI

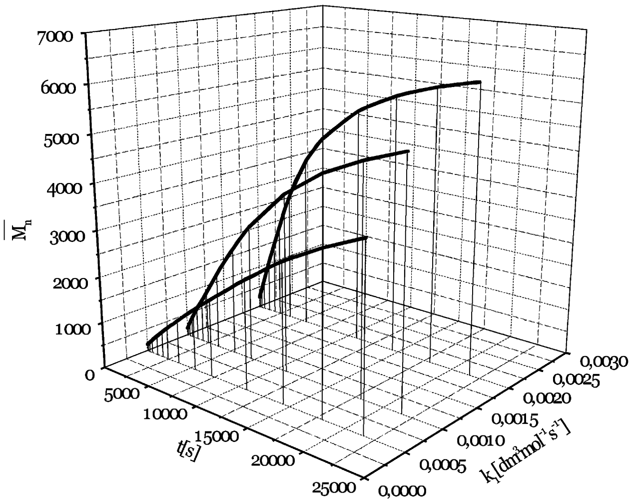

Fig. 1. Graphical presentation of model relationships between molecular weight ($\bar{M}_n$) of PU and time at the fixed reaction constant (k_1) in polyaddition of TDI to 1,4-BD ($r = 1$).

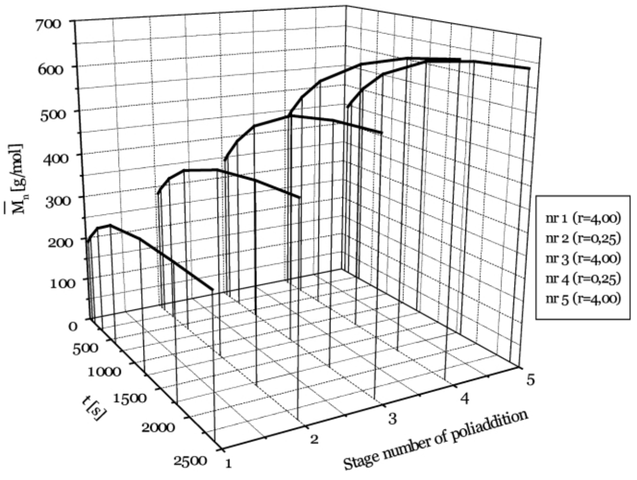

Fig. 2. Molecular weight ($\bar{M}_n$) of PU in relation to the number of the step/stage in polyaddition of TDI to POG-200 ($k_1 = 0.0005$ dm^3 mol^{-1} s^{-1}, $r = 4$).

with 1,4-BD, in relation to the value of k_1. Fig. 2 shows the simulation results for the urethane oligomers production process which has been based on the reaction of TDI and POG 200, with the reaction proceeding with no external catalyst at about 55 °C. The simulation was limited to cover 5–6 stages which were then implemented in practice [18]. The calculation results were helpful in designing a multi-stage method for the synthesis of urethane oligomers.

3. Experimental

3.1. Raw materials and reagents

- 2,4- and 2,6-Tolylene diisocyanate (TDI). A commercial product was used in the study. It was a mixture of 2,4-TDI and 2,6-TDI isomers at the ratio of 80 and 20%, respectively, from Aldrich.
- Polyoxyethylene glycol (POG) with $\bar{M}_n = 200, 300, 400$, 600 and 1000 g/mol, from Aldrich. The glycols were dried under vacuum in N_2, at temp. 110 °C, during 2 h.
- Polycaprolactone diol (PCD) with $\bar{M}_n = 530$ and 1250, from Aldrich.
- Benzoyl chloride (pure), from POCh-Gliwice, Poland.
- 1,4-Butanediol (BD) (pure), from Aldrich.
- The solvents: hexane, ethyl acetate, toluene, xylene, carbon tetrachloride, and tetrahydrofuran were reagent grade materials, supplied by POCh-Gliwice, Poland.

3.2. Method for the synthesis of urethane oligomers

The reactions were carried out in bulk in a glass reactor, under nitrogen. Benzoyl chloride was used (0.3 wt% with respect to TDI) as a viscosity control agent; moreover, its use made it possible to expand the stability period of synthesised prepolymers A_nB_{n+1} and hence the prepolymers could be employed as parent substances in subsequent reactions. The polyaddition process was always initiated by

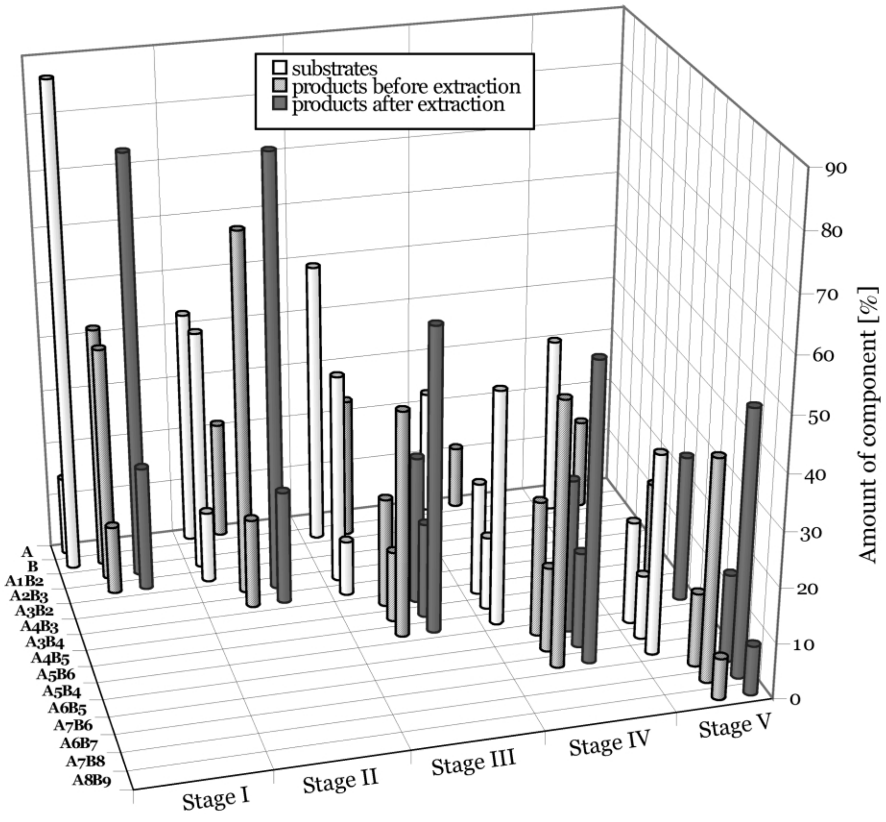

Fig. 3. Chemical compositions for raw materials and products of successive reactions of BD and TDI.

Table 1
Specifications for the reactions which yield urethane oligomers

Symbol of oligomer	No. for polyaddition stage	Basic reaction in polyaddition stage	Polyol component	Extraction solvent system for excess monomer
I-BDa	I	$A + 4B \rightarrow A_1B_2 + 2B$	BD	–
I-BDb			BD	Hexane/ethyl acetate (2:1)
I-200a			POG 200	–
I-200b			POG 200	Hexane/ethyl acetate (2:1)
I-300a			POG 300	–
I-300b			POG 300	Hexane/eth. acetate (1.5:1)
I-400a			POG 400	–
I-400b			POG 400	Hexane/eth. acetate (1.5:1)
I-600a			POG 600	–
I-600b			POG 600	Hexane/ethyl acetate (1:1)
I-1000a			POG 1000	–
I-1000b			POG 1000	Hexane/ethyl acetate (1:1)
I-530a			PCD 530	–
I-530b			PCD 530	Hexane/ethyl acetate (1:1)
I-1250a			PCD 1250	–
I-1250b			PCD 1250	Hexane/ethyl acetate (1:1)
II-BDa	II	$A_1B_2 + 4A \rightarrow A_3B_2 + 2A$	BD	–
II-BDb			BD	water
II-200a			POG 200	–
II-200b			POG 200	Toluene
II-300a			POG 300	–
II-300b			POG 300	Toluene
II-400a			POG 400	–
II-400b			POG 400	Toluene
II-600a			POG 600	–
II-600b			POG 600	Toluene–xylene
II-1000a			POG 1000	–
II-1000b			POG 1000	CCl_4
II-530a			PCD 530	–
II-530b			PCD 530	Toluene–xylene
II-1250a			PCD 1250	–
II-1250b			PCD 1250	CCl_4
III-BDa	III	$A_3B_2 + 4B \rightarrow A_3B_4 + 2B$	BD	Like at stage I
III-BDb			BD	
III-200a			POG 200	
III-200b			POG 200	
III-300a			POG 300	
III-300b			POG 300	
III-400a			POG 400	
III-400b			POG 400	
III-600a			POG 600	
III-600b			POG 600	
III-1000a			POG 1000	
III-1000b			POG 1000	
III-530a			PCD 530	
III-530b			PCD 530	
III-1250a			PCD 1250	
III-1250b			PCD 1250	
IV-BDa	IV	$A_3B_4 + 4A \rightarrow A_5B_4 + 2A$	BD	Like at stage II
IV-BDb			BD	
IV-200a			POG 200	
IV-200b			POG 200	
IV-300a			POG 300	
IV-300b			POG 300	
IV-400a			POG 400	
IV-400b			POG 400	
IV-600a			POG 600	
IV-600b			POG 600	
IV-1000a			POG 1000	
IV-1000b			POG 1000	

Table 1 (*continued*)

Symbol of oligomer	No. for polyaddition stage	Basic reaction in polyaddition stage	Polyol component	Extraction solvent system for excess monomer
IV-530a			PCD 530	
IV-530b			PCD 530	
IV-1250a			PCD 1250	
IV-1250b			PCD 1250	
V-BDa	V	$A_5B_4 + 4B \rightarrow A_5B_6 + 2B$	BD	Like at stage I
V-BDb			BD	
V-200a			POG 200	
V-200b			POG 200	
V-300a			POG 300	
V-300b			POG 300	
V-400a			POG 400	
V-400b			POG 400	
V-600a			POG 600	
V-600b			POG 600	
V-1000a			POG 1000	
V-1000b			POG 1000	
V-530a			PCD 530	
V-530b			PCD 530	
V-1250a			PCD 1250	
V-1250b			PCD 1250	

a reaction which proceeded at a considerable excess of diisocyanate (B). In order to make the complete conversion possible for the parent substances A or B which were in short supply, each reaction - what can be observed in diagram (2)—was carried out at 100% excess of the other reacting substance—BD, POG, PCD or TDI. The feeds were introduced under possibly mild conditions to avoid any uncontrolled conversion of –NCO groups which were still present in the system to allophanates or their cyclisation to isocyanurates. No external catalyst was employed in our experiments. A calculated amount of hydroxyl-terminated or isocyanate-terminated oligomer prepared at an earlier stage was introduced dropwise to TDI or to appropriate glycol, respectively. It was always the minor component that was introduced to the component which was present in excess. The time of introduction was adjusted to last ca. 30 min. The reacting mixture was maintained at 65 ± 1 °C. The temperature was kept at that level for another 2 h after the predefined volume of the minority component had been added. Extraction was employed to remove excess unconverted monomer after every stage and thus purified intermediate A_nB_m could be employed as a parent substance for another polyaddition stage.

The principal reactions for every stage I–V are presented in Table 1. The letter a denotes the samples taken directly from the reactor, while the b denotes the products after extracting out the excess of TDI or diol.

On the basis of assumed reaction stoichiometry and experimentally determined content of free –NCO groups we could calculate the compositions of initial mixtures, i.e. weight fractions for substrates (A_nB_{n+1} and B at odd stages 1, 3, 5, as well as $A_{n+1}B_n$ and A at even stages 2 and 4 of the processes) and for reaction products. In case of even stages 2 and 4, the course of reaction—which conformed to our expectations—and hence the expected chemical compositions of the urethane–hydroxyl oligomers formed was confirmed indirectly by comparing the theoretical and experimental losses in weight for samples after excess monomer A had been extracted out of them.

Exemplary compositions of mixtures at successive stages of the reaction between BD and TDI are shown diagrammatically in Fig. 3.

3.3. Example I—synthesis of urethane oligomers from TDI and BD

I stage. In a 1 dm^3 jacketed glass reactor fitted with reflux condenser, stirrer and nitrogen inlet tube TDI (696.68 g, 4 M) and benzoyl chloride (2.09 g, 0.3 wt%) was charged. After heating the reaction mixture to 65 ± 1 °C, BD (90.00 g, 1 M) was added drop by drop in the time of 30 min. Then the heating was continued 2 h in order to supply total BD conversion. After the end of the reaction, precipitate of the product (I-BDa) was washed by the mixture *n*-hexane and ethyl acetate equal 2:1. The concentration of –NCO groups after the end of extraction amount 36.32% (theoretically: 39.43%). The obtained product I-BDb was dried under a vacuum in the time of 15 min and then used as a substrate in the next stage.

II stage. In a 1 dm^3 jacketed glass reactor BD (300.29 g, 3.34 M) and benzoyl chloride (0.12 g, 0.3 wt% to I-BDb). After heating the reaction mixture to 65 ± 1 °C, I-BDb (400.00 g, 0.834 M) was added drop by drop in the time of 30 min. Then, heating was continued 2 h. The obtained product (II-BDa) was in the form of very sticky liquid. Very little amount of THF was added to it in order to make the extraction easier. Unreacted excess of BD was extracted by water. The extraction was carried out to get constant weight of the sample according to theoretical dates (580.00 g; 0.834 M). At the end of the extraction, the product was dried under a vacuum at 90 °C in 15 min. The product II-BDb was a hard and transparent resin.

III stage. The reaction was carried out analogous to the I stage 300.00 g (0.50 M) II-BDb and 348.34 g (2.00 M) TDI were used. The concentration of the –NCO groups in the final product after extraction (III-BDb) amounted to 14.28% (theoretically: 17.28%).

IV stage. The reaction was carried out analogous to the II stage. 300.00 g (0.246 M) III-BDb and 88.55 g (0.984 M) BD were used. The extraction was carried out by water till constant weight 344.27 g (0.246 M) of the product (V-BDb).

V stage. Analogous to the I or III stage.

3.4. Example II—synthesis of urethane oligomers from TDI and PEG 200

I stage. In a 1 dm^3 jacketed glass reactor fitted with reflux condenser, stirrer and nitrogen inlet tube TDI (348.34 g, 2 M) and benzoyl chloride (1.05 g, 0.3 wt%) was charged. After heating the reaction mixture to 65 ± 1 °C, PEG 200 (100,00 g, 0.5 M) was added drop by drop in 30 min. Then, heating was continued 2 h in order to supply total glycol conversion. At the end of the reaction, liquid product (I-200a) was extracted by the mixture *n*-hexane and ethyl acetate equal 2:1. At the end of extraction, the rest of the product (I-200b) was evaporated under vacuum. The concentration of –NCO groups after the completion of extraction amounts to 27.06% (theoretically: 31.76%).

II stage. In a 1 dm^3 jacketed glass reactor PEG 200 (372.88 g, 1.86 M) and benzoyl chloride (0.9 g, 0.3 wt% to I-200b). After heating the reaction mixture to 65 ± 1 °C, 300.00 g (0.47 M) I-200b was added in 30 min. Then, the heating was continued for 2 h. The obtained product was in a form of sticky liquid. Unreacted excess of PEG 200 was extracted by toluene. The extraction was carried out to getting the weight of sample as theoretical one (486.44 g, 0.47 M). At the end of the extraction, the rest of toluene was evaporated under vacuum. The product (II-200b) was obtained in the form of sticky liquid.

III and V stage. Analogous to the I stage.

IV stage. Analogous to the II stage.

3.5. Analytical methods

Concentration of NCO groups. The typical dibutylamine method was employed. Excess of unreacted dibutylamine was titrated with aqueous HCl against bromophenol blue [19].

Viscosity measurements. Dynamic viscosity of oligomers A_nB_m was determined at 25 °C with the use of a rotational Rheotest 2 viscometer (Rheotest GmbH). Cylinders of H type were used at the revolution range of 3b to 12a (range I), depending on the type of product. No dependence of viscosity on shear rate was observed in practice.

Structural analysis. IR spectra were recorded on a Spekord M60 apparatus (Zeiss, Germany). The samples were in the form of a thin film on polyethylene substrate.

Mass spectrometry (*MS*). The mass spectra of the resulting polyurethane oligomers were recorded on an electrospray ionisation spectrometer (ESI MS) Finnigan MAT 95S (Germany) and on a MALDI MS spectrometer. ESI spectra were obtained by using KJ solution for ionisation. The mobile phase ($CH_3OH + THF$) flow rate was set up at 5 μdm^3/min. Only the positive ions were recorded in the range of 200–2000 *M*/*z*; their molecular weight specifications were enlarged by the mass of K^+ (39) or Na^+ (22) originating essentially from impurities. The samples were diluted with methanol to the concentration of pmol/dm^3.

MALDI spectra were recorded on a Voyager-Elite (Perseptive Biosystems, USA) apparatus in linear mode with delayed ion extraction. The instrument was equipped with N_2 laser (337 nm) and the matrix was 2,5-dihydroxybenzoic acid (DHB, $M = 153$ g/mol) dissolved in THF (10 mg/cm^3). The samples were also dissolved in THF (to concentration of 1 mg/cm^3) and NaI in acetone (10 mg/cm^3) was added. The ions with the mass increased by molecular weights of Na or K were recorded.

Gel permeation chromatography (*GPC*). The GPC apparatus used was a Viscotec T60A equipped with a triple detector: RI, light scattering (LS) and viscosity detector (DV). Separations were made at 30 ± 0.1 °C on a $GMH_{HR}L$ column (size 7.8 mm × 300 mm) packed with TSK-gel of pore diameter 5 μm from Thoso-Haas, and Styragel 1 and 2 (size 7.8 mm × 300 mm) from Waters. The eluent (THF) flow rate was 1 cm^3/min, volume of inflow circuit—20 μdm^3. Operation of the chromatograph was controlled by original computer software *TRISEC Data Acquisition System* by Viscotec Corporation; deconvolution was possible for individual peaks which corresponded to non-homogeneous oligomers. The results were interpreted on the basis of conventional calibration of columns with carbamate standards which had been synthesised especially for that purpose. Chromatographic analysis of standards yielded the calibration relation for logarithm of mass versus retention volume.

$$\log M = -0.1595\, V_{\mathrm{ret}} + 6.8219 \quad (3)$$

The differential curves for distribution of molecular weights as obtained from sample elution curves and from the calibration equation (3) were presented in the form of standardized charts: *detector signal divided by the total area below the chromatogram - molecular weights of components*. The internal standardization method was employed to find quantitative compositions of prepolymers from thus obtained chromatograms. A special computer software Peak Fit v4 was utilised for that purpose which attributed

Table 2
Interpretation for GPC chromatograms of monomers and urethane prepolymers

Symbol of oligomer	M_n as per MWD curves	Compound	Theoretical molecular weight (g/mol)	Amount of component as calculated by standardisation of GPC chromatograms (wt%)	Amount of component as calculated from reaction mass balance (wt%)	$PD = \bar{M}_w/\bar{M}_n$
BD	96.9	A	90	100		1.00
I-BDb	177.7	B	174.17	8.03		1.05
	459.6	$A_1B_2 + 2CH_3OH$[a]	502.34	87.49	77.18	
	748.9	$A_2B_3 + 2CH_3OH$	766.51	4.47	22.82	
II-BDb	350.6	A_2B_1	354.17	6.92		1.16
	617.6	A_3B_2	618.34	65.96	79.16	
	884.5	A_4B_3	882.51	9.22	20.84	
	1146.1	A_5B_4	1146.68	13.34		
	1390.2	A_6B_5	1410.85	2.57		
	1633.7	A_7B_6	1675.02	1.99		
III-BDb	182.1	B	174.17	4.12		1.30
	267.6	$B + 2CH_3OH$	238.17	4.86	27.00	
	761.0	$A_2B_3 + 2CH_3OH$	766.51	7.93	17.42	
	862.3	$A_3B_3 + CH_3OH$	824.51	4.49	55.60	
	1036.1	$A_3B_4 + 2CH_3OH$	1030.68	53.09		
	1310.9	$A_4B_5 + 2CH_3OH$	1294.85	9.54		
	1570.1	$A_5B_6 + 2CH_3OH$	1559.02	9.12		
	1817.7	$A_6B_7 + 2CH_3OH$	1823.19	6.85		
IV-BDb	178.2			6.03		1.62
	378.7	A_2B_1	354.17	0.80	27.91	
	894.1	A_4B_3	882.51	6.43	17.39	
	1148.1	A_5B_4	1146.68	33.95	54.28	
	1419.6	A_6B_5	1410.85	8.62		
	1665.4	A_7B_6	1675.02	9.33		
	1925.0	A_8B_7	1939.19	7.72		
	2161.6	A_9B_8	2203.36	8.95		
	2464.6	$A_{10}B_9$	2467.53	11.43		
	2807.3	$A_{11}B_{10}$	2731.70	6.71		
V-BDb	162.5	B	174.17	1.78		1.28
	727.5	$A_2B_3 + 2CH_3OH$	766.51	0.92	26.80	
	995.6	$A_3B_4 + 2CH_3OH$	1030.68	1.84	15.98	
	1190.7	$A_4B_5 + 2CH_3OH$	1294.85	4.58	48.28	
	1418.7	$A_5B_6 + 2CH_3OH$	1559.02	39.47	8.93	
	1705.1	$A_6B_7 + 2CH_3OH$	1823.19	9.46		
	1932.0	$A_7B_8 + 2CH_3OH$	2087.36	9.84		
	2190.1	$A_8B_8 + CH_3OH$	2145.36	11.48		
	2435.1	$A_8B_9 + 2CH_3OH$	2351.53	4.41		
	2731.0	$A_9B_{10} + 2CH_3OH$	2615.70	3.02		
	3062.2	$A_{10}B_{11} + 2CH_3OH$	2879.87	2.62		

(*continued on next page*)

Table 2 (*continued*)

Symbol of oligomer	M_n as per MWD curves	Compound	Theoretical molecular weight (g/mol)	Amount of component as calculated by standardisation of GPC chromatograms (wt%)	Amount of component as calculated from reaction mass balance (wt%)	$PD = \bar{M}_w/\bar{M}_n$
	3455.7	$A_{11}B_{12} + 2CH_3OH$	3144.04	2.15		
POG200	105.0	A	106 ($n = 2$)	4.89		1.07
	117.8	A		46.54		
	152.9	A	150 ($n = 3$)	23.63		
	186.3	A	194 ($n = 4$)	14.95		
	214.7	A	238 ($n = 5$)	7.46		
	230.1		282 ($n = 6$)	2.53		
I-200b	170.5	B	174.17	20.00		1.31
	260.6	$B + 2CH_3OH$	238.17	4.33	63.51	
	529.0	$A_1B_2 + 2CH_3OH$	562.34 ($n_1 = 3$)	65.65	36.49	
	889.0	$A_2B_3 + 2CH_3OH$	886.51 ($n_{1,2} = 3$)	10.02		
II-200b	359.3			0.94		1.36
	513.3	A_2B_1	562.17 ($n_{1,2} = 4$)	5.65	67.75	
	901.0	A_3B_2	886.34 ($n_1 = 3$, $n_{2,3} = 4$)	24.83	32.25	
	1305.1	A_4B_3	1298.51 ($n_{1-4} = 4$)	16.65		
	1673.0	A_5B_4	1666.68 ($n_{1-5} = 4$)	21.66		
	2088.8	A_6B_5	2078.85 ($n_{1-5} = 4$, $n_6 = 5$)	16.25		
	2520.8	A_7B_6	2535.02 ($n_{1-4} = 4$, $n_{5-7} = 5$)	12.44		
	3072.9	A_8B_7	3079.19 ($n_1 = 4$, $n_{2-8} = 5$)	1.58		
III-200b	187.8	$B + 2CH_3OH$	238.17	1.00		1.43
	595.1	$A_1B_2 + 2CH_3OH$	606.34 ($n_1 = 4$)	2.52	36.46	
	962.5	$A_2B_3 + 2CH_3OH$	974.51 ($n_{1,2} = 4$)	4.58	16.04	
	1361.7	$A_3B_4 + 2CH_3OH$	1342.68 ($n_{1-3} = 4$)	5.47	47.50	
	1752.8	$A_4B_5 + 2CH_3OH$	1754.85 ($n_{1-3} = 4$, $n_4 = 5$)	28.06		
	2121.3	$A_5B_6 + 2CH_3OH$	2123.02 ($n_{1-4} = 4$, $n_5 = 5$)	27.15		
	2668.4	$A_6B_7 + 2CH_3OH$	2667.19 ($n_1 = 4$, $n_{2-6} = 5$)	20.64		
	3519.1	$A_7B_8 + 2CH_3OH$	3497.53 ($n_{1-7} = 5$)	10.58		
IV-200b	105.9	A	106 ($n = 2$)	1.26		1.50
	482.6	A_2B_1	474.17 ($n_{1,2} = 3$)	1.64	38.36	
	846.6	A_3B_2	886.34 ($n_1 = 3$, $n_{2,3} = 4$)	2.05	15.98	
	1157.3	A_4B_3	1166.51 ($n_{1-3} = 3$, $n_4 = 4$)	1.94	45.66	
	1587.0	A_5B_4	1578.68 ($n_{1,2} = 3$, $n_{3-5} = 4$)	14.13		
	2029.3	A_6B_5	2034.85 ($n_{1-6} = 4$)	10.03		
	2400.1	A_7B_6	2403.02 ($n_{1-7} = 4$)	17.56		
	2979.1	A_8B_7	2947.19 ($n_{1-4} = 4$, $n_{5-8} = 5$)	20.25		
	3860.4	$A_{11}B_{10}$	3875.70 ($n_{1-11} = 4$)	19.24		
	5276.8	$A_{14}B_{13}$	5282.38 ($n_{1-8} = 4$, $n_{9-14} = 5$)	11.89		
V-200b	326.5	$B + 2CH_3OH$	238.17	0.36		1.29
	629.10	$A_1B_2 + 2CH_3OH$	606.34 ($n_1 = 4$)	1.77	28.90	
	1058.0	$A_2B_3 + 2CH_3OH$	1062.51 ($n_{1,2} = 4$)	2.14	11.67	
	2177.9	$A_5B_6 + 2CH_3OH$	2167.02 ($n_{1-3} = 4$, $n_{4,5} = 5$)	11.15	32.61	

Table 2 (*continued*)

Symbol of oligomer	M_n as per MWD curves	Compound	Theoretical molecular weight (g/mol)	Amount of component as calculated by standardisation of GPC chromatograms (wt%)	Amount of component as calculated from reaction mass balance (wt%)	$PD = \bar{M}_w/\bar{M}_n$
		A_6B_7	2383.19 ($n_{1-6} = 4$)		26.82	
		A_7B_8	2751.36 ($n_{1-7} = 4$)			
	3175.6	$A_8B_9 + 2CH_3OH$	3183.53 ($n_{1-8} = 4$)	15.89		
	4369.2	$A_{11}B_{12} + 2CH_3OH$	4376.04 ($n_{1-9} = 4$, $n_{10-12} = 5$)	21.78		
	5814.6	$A_{15}B_{16} + 2CH_3OH$	5804.72 ($n_{1-14} = 4$, $n_{15} = 5$)	20.44		
	7230.1	$A_{19}B_{20} + 2CH_3OH$	7233.40 ($n_{1-19} = 4$)	26.47		
POG300	130.3	A	150 ($n = 3$)	10.30		1.02
	164.9	A	194 ($n = 4$)	13.79		
	215.3	A	238 ($n = 5$)	17.64		
	260.4	A	282 ($n = 6$)	17.89		
	303.0	A	326 ($n = 7$)	16.11		
	343.8	A	370 ($n = 8$)	11.78		
	387.7	A	414 ($n = 9$)	7.25		
	456.6	A	458 ($n = 10$)	5.24		
I-300b	207.6	$B + 2CH_3OH$	238.17	2.20		1.12
	607.2	$A_1B_2 + 2CH_3OH$	650.34 ($n = 5$)	82.83	66.40	
	1032.7	$A_2B_3 + 2CH_3OH$	1062.51 ($n = 5$)	14.97	33.60	
II-300b	1245.6	A_3B_2	1238.34 ($n_{1,2} = 6$, $n_3 = 7$)	35.50	71.27	1.19
	1667.6	A_4B_3	1694.51 ($n_{1-3} = 6$, $n_4 = 7$)	10.18	28.73	
	2072.3	A_5B_4	2106.68 ($n_{1-5} = 6$)	28.94		
	2661.5	A_6B_5	2694.85 ($n_{1-3} = 6$, $n_{4-6} = 7$)	15.47		
	3212.3	A_7B_6	3239.02 ($n_{1,2} = 6$, $n_{3-7} = 7$)	6.93		
	3778.5	A_8B_7	3783.19 ($n_1 = 6$, $n_{2-8} = 7$)	2.98		
III-300b	539.0			3.26		1.21
	890.1	$A_1B_2 + 2CH_3OH$	826.34 ($n_1 = 9$)	3.82	46.03	
	1250.1	$A_2B_3 + 2CH_3OH$	1238.51 ($n_{1,2} = 7$)	28.49	16.95	
	1618.7	$A_3B_4 + 2CH_3OH$	1606.68 ($n_{1-3} = 6$)	12.55	37.02	
	1928.4	$A_4B_5 + 2CH_3OH$	1930.85 ($n_{1-3} = 5$, $n_4 = 6$)	21.20		
	2340.5	$A_5B_6 + 2CH_3OH$	2343.02 ($n_{1-4} = 5$, $n_5 = 6$)	15.19		
	2784.5	$A_6B_7 + 2CH_3OH$	2799.19 ($n_{1-4} = 5$, $n_{5-6} = 6$)	10.51		
	3315.5	$A_7B_8 + 2CH_3OH$	3343.36 ($n_{1-2} = 5$, $n_{3-7} = 6$)	4.97		
IV-300b	259.1	A	282 ($n = 6$)	1.89		1.25
	1240.8	A_3B_2	1238.34 ($n_{1,2} = 6$, $n_3 = 7$)	2.40	48.38	
	1797.5	A_4B_3	1782.51 ($n_1 = 6$, $n_{2-4} = 7$)	17.78	16.71	
	2282.0	A_5B_4	2194.68 ($n_{1-3} = 6$, $n_{4-5} = 7$)	25.66	34.94	
	2733.8	A_6B_5	2694.85 ($n_{1-3} = 6$, $n_{4-6} = 7$)	31.67		
	3261.0	A_7B_6	3151.02 ($n_{1-4} = 6$, $n_{5-7} = 7$)	20.60		
V-300b	180.00	$B + 2CH_3OH$	238.17	3.42		1.53
	1753.4	$A_3B_4 + 2CH_3OH$	1738.68 ($n_{1-3} = 7$)	3.26	15.32	
	2387.0	$A_5B_6 + 2CH_3OH$	2387.02 ($n_{1-3} = 5$, $n_{4-5} = 6$)	12.46	5.16	

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Table 2 (*continued*)

Symbol of oligomer	M_n as per MWD curves	Compound	Theoretical molecular weight (g/mol)	Amount of component as calculated by standardisation of GPC chromatograms (wt%)	Amount of component as calculated from reaction mass balance (wt%)	$PD = \bar{M}_w/\bar{M}_n$
	3017.2	$A_6B_7 + 2CH_3OH$	2975.19 ($n_{1-6} = 6$)	21.63	10.61	
	3732.1	$A_7B_8 + 2CH_3OH$	3739.36 ($n_{1-7} = 7$)	29.04	68.90	
		A_8B_9	3823.53 ($n_{1-8} = 6$)			
	4442.9	$A_9B_{10} + 2CH_3OH$	4455.70 ($n_{1-5} = 6$, $n_{6-9} = 7$)	30.21		
POG400	79.5	A	106 ($n = 2$)	0.98		1.12
	133.4	A	150 ($n = 3$)	5.44		
	179.7	A	194 ($n = 4$)	10.03		
	226.0	A	238 ($n = 5$)	14.67		
	270.8	A	282 ($n = 6$)	17.46		
	314.2	A	326 ($n = 7$)	17.00		
	357.5	A	370 ($n = 8$)	14.06		
	401.9	A	414 ($n = 9$)	10.23		
	451.6	A	458 ($n = 10$)	6.34		
	514.2	A	502 ($n = 11$)	3.78		
I-400b	201.9	$B + 2CH_3OH$	238.17	1.23		1.24
	811.9	$A_1B_2 + 2CH_3OH$	826.17 ($n_1 = 9$)	75.16	82.87	
	1413.7	$A_2B_3 + 2CH_3OH$	1414.51 ($n_{1,2} = 9$)	23.60	17.13	
II-400b	316.4	A	326 ($n = 7$)	1.51		1.60
	858.0	A_2B_1	870.17 ($n_1 = 7$, $n_2 = 8$)	10.87	86.19	
	1527.1	A_3B_2	1502.34 ($n_{1,2} = 8$, $n_3 = 9$)	36.46	13.82	
	2114.8	A_4B_3	2090.51 ($n_{1,2} = 8$, $n_{3,4} = 9$)	23.50		
	2704.4	A_5B_4	2678.68 ($n_{1,2} = 8$, $n_{3-5} = 9$)	20.41		
	3450.5	A_6B_5	3442.85 ($n_{1-4} = 9$, $n_{5,6} = 10$)	7.24		
III-400b	108.1	B	174.17	1.34		1.67
	862.1	$A_1B_2 + 2CH_3OH$	870.17 ($n_1 = 10$)	13.97	81.06	
	2078.3	$A_3B_4 + 2CH_3OH$	2046.68 ($n_{1,2} = 9$, $n_3 = 10$)	43.78	12.34	
	3005.0	A_4B_5	2526.85 ($n_{1-4} = 9$)	40.92	6.60	
		$A_5B_6 + 2CH_3OH$	3003.02 ($n_{1-4} = 8$, $n_5 = 9$)			
IV-400b	319.7	A	326 ($n = 7$)	2.31		1.30
	439.2	A	458 ($n = 10$)	2.32		
	923.2	A_2B_1	914.17 ($n_{1,2} = 8$)	4.76		
	1534.5	A_3B_2	1502.34 ($n_{1,2} = 8$, $n_3 = 9$)	3.94		
	2118.3	A_4B_3	2090.51 ($n_{1,2} = 8$, $n_{3,4} = 9$)	22.46		
	2850.5	A_5B_4	2854.68 ($n_{1-3} = 9$, $n_{4,5} = 10$)	22.74	82.38	
	3544.6	A_6B_5	3530.85 ($n_{1,2} = 9$, $n_{3-6} = 10$)	24.13	11.67	
		A_7B_6	3943.02 ($n_{1-7} = 9$)		5.95	
	4363.5	A_8B_7	4355.02 ($n_{1-4} = 8$, $n_{5-8} = 9$)	17.34		
V-400b	756.5	$A_1B_2 + 2CH_3OH$	782.17 ($n_1 = 8$)	1.17		1.39
	2136.6	$A_3B_4 + 2CH_3OH$	2134.68 ($n_{1-3} = 10$)	4.28		
	3074.1	$A_5B_6 + 2CH_3OH$	3047.02 ($n_{1-3} = 8$, $n_{4,5} = 9$)	21.43	41.97	
	4623.5	A_6B_7	3703.19 ($n_{1-6} = 9$)		5.82	

Table 2 (*continued*)

Symbol of oligomer	M_n as per MWD curves	Compound	Theoretical molecular weight (g/mol)	Amount of component as calculated by standardisation of GPC chromatograms (wt%)	Amount of component as calculated from reaction mass balance (wt%)	$PD = \bar{M}_w/\bar{M}_n$
		$A_7B_8 + 2CH_3OH$	4619.36 ($n_1 = 9$, $n_{2-7} = 10$)	73.12	2.92	
		A_8B_9	4879.53 ($n_{1-8} = 9$)		49.29	
POG 600	534.8	A	546 ($n = 12$)	100		1.03
I-600b	264.2	$B + 2CH_3OH$	238.17	3.93		1.21
	1014.9	$A_1B_2 + 2CH_3OH$	1002.34 ($n_1 = 13$)	76.92	88.97	
	1792.2	$A_2B_3 + 2CH_3OH$	1766.51 ($n_{1,2} = 13$)	16.67	11.03	
	2456.4	$A_3B_4 + 2CH_3OH$	2442.68 ($n_{1,2} = 12$, $n_3 = 13$)	2.49		
II-600b	557.2	A	546 ($n = 12$)	13.24		1.66
	2188.2	A_3B_2	2162.34 ($n_{1,2} = 13$, $n_3 = 14$)	38.20	91.50	
	2907.8	A_4B_3	2882.51 ($n_{1-4} = 13$)	9.36	8.50	
	3600.2	A_5B_4	3602.68 ($n_1 = 12$, $n_{2-5} = 13$)	25.70		
	4543.5	A_6B_5	4542.85 ($n_{1-3} = 13$, $n_{4-6} = 14$)	13.50		
III-600b	186.6	$B + 2CH_3OH$	238.17	0.81		1.64
	1045.7	$A_1B_2 + 2CH_3OH$	1046.34 ($n_1 = 14$)	5.38	33.74	
	1747.6	$A_2B_3 + 2CH_3OH$	1766.51 ($n_{1,2} = 13$)	5.29	3.02	
	2635.7	$A_3B_4 + 2CH_3OH$	2618.68 ($n_1 = 13$, $n_{2,3} = 14$)	31.38	63.24	
		A_4B_5	3230.85 ($n_{1-4} = 13$)			
	3843.6	$A_5B_6 + 2CH_3OH$	3839.02 ($n_{1-4} = 12$, $n_5 = 13$)	20.36		
	5081.6	$A_6B_7 + 2CH_3OH$	5087.19 ($n_{1-6} = 14$)	36.77		
IV-600b	516.6	A	546 ($n = 12$)	5.28		1.50
	1306.5	A_2B_1	1310.17 ($n_1 = 12$, $n_2 = 13$)	6.89	36.69	
	2244.9	A_3B_2	2250.34 ($n_{1-3} = 14$)	7.59	3.05	
	3010.9	A_4B_3	3014.51 ($n_1 = 13$, $n_{2-4} = 14$)	9.65	60.26	
	3892.4	A_5B_4	3866.68 ($n_{1-5} = 14$)	15.18		
		A_6B_5	4410.85 ($n_{1-6} = 13$)	19.67		
	4939.2	A_7B_6	4955.02 ($n_{1-5} = 12$, $n_{6,7} = 13$)			
	6123.5	A_8B_7	6115.19 ($n_{1-4} = 13$, $n_{5-8} = 14$)	35.71		
V-600b	1091.6	$A_1B_2 + 2CH_3OH$	1090.34 ($n_1 = 15$)	0.46		1.23
	1798.9	$A_2B_3 + 2CH_3OH$	1766.51 ($n_{1,2} = 13$)	1.55		
	2698.5	$A_3B_4 + 2CH_3OH$	2662.68 ($n_{1-3} = 14$)	4.47		
	3228.8	$A_4B_5 + 2CH_3OH$	3250.85 ($n_1 = 12$, $n_{2-4} = 13$)	11.65		
	4274.3	$A_5B_6 + 2CH_3OH$	4235.02 ($n_1 = 13$, $n_{2-5} = 14$)	22.21	8.70	
		A_6B_7	4759.19 ($n_{1-6} = 13$)		0.71	
	5692.6	$A_7B_8 + 2CH_3OH$	5675.36 ($n_{1-5} = 13$, $n_{6,7} = 14$)	29.21	13.93	
	6404.4	$A_8B_9 + 2CH_3OH$	6395.53 ($n_{1-7} = 13$, $n_8 = 14$)	30.45	76.65	
POG 1000	1092.5	A	1074 ($n = 24$)	100		1.10
I-1000b	276.4	$B + 2CH_3OH$	238.17	2.79		1.37
	768.9			2.40		
	1448.4	$A_1B_2 + 2CH_3OH$	1442.34 ($n_1 = 23$)	63.79	67.08	

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Table 2 (*continued*)

Symbol of oligomer	M_n as per MWD curves	Compound	Theoretical molecular weight (g/mol)	Amount of component as calculated by standardisation of GPC chromatograms (wt%)	Amount of component as calculated from reaction mass balance (wt%)	$PD = \bar{M}_w/\bar{M}_n$
	2473.2	$A_2B_3 + 2CH_3OH$	2470.51 ($n_{1,2} = 21$)	23.97	32.92	
	3294.5	$A_3B_4 + 2CH_3OH$	3586.68 ($n_{1-3} = 21$)	7.06		
II-1000b	357.0			2.27		1.35
	907.4	A	942 ($n = 21$)	3.80		
	2367.4	A_2B_1	2322.17 ($n_{1,2} = 24$)	13.40		
	3235.1	A_3B_2	3218.34 ($n_{1,2} = 21$, $n_3 = 22$)	32.50	73.84	
	4329.6	A_4B_3	4378.51 ($n_{1,2} = 21$, $n_{3,4} = 22$)	28.72	26.16	
	5456.8	A_5B_4	5450.68 ($n_{1-4} = 21$, $n_5 = 22$)	19.31		
III-1000b	197.6	$B + 2CH_3OH$	238.17	3.15		1.35
	1398.5	$A_1B_2 + 2CH_3OH$	1398.34 ($n_1 = 22$)	6.74		
	2467.2	$A_2B_3 + 2CH_3OH$	2470.51 ($n_{1,2} = 21$)	11.07		
	3575.1	$A_3B_4 + 2CH_3OH$	3586.68 ($n_{1-3} = 21$)	24.54	43.21	
	4836.9	$A_4B_5 + 2CH_3OH$	4878.85 ($n_{1-4} = 22$)	26.21	14.93	
	6306.7	$A_5B_6 + 2CH_3OH$	6303.02 ($n_{1-4} = 23$, $n_5 = 24$)	28.29	41.86	
IV-1000b	1937.2	A_2B_1	2058.17 ($n_{1,2} = 21$)	3.02		1.44
	3019.1	A_3B_2	3174.34 ($n_{1-3} = 21$)	8.82		
	4501.6	A_4B_3	4510.51 ($n_{1-3} = 22$, $n_4 = 23$)	12.09		
	5618.9	A_5B_4	5626.68 ($n_{1-5} = 22$)	21.26	46.45	
	6752.8	A_6B_5	6786.85 ($n_{1-6} = 22$)	22.42	14.68	
	8024.5	A_7B_6	8035.02 ($n_{1-5} = 22$, $n_{6,7} = 23$)	32.40	38.86	
V-1000b	375.4	$B + 2CH_3OH$	238.17	4.08		2.37
	2068.8	$A_2B_3 + 2CH_3OH$	2470.51 ($n_{1,2} = 21$)	7.55		
	3295.8	$A_3B_4 + 2CH_3OH$	3586.68 ($n_{1-3} = 21$)	10.45		
	4571.8	$A_4B_5 + 2CH_3OH$	4702.85 ($n_{1-4} = 21$)	25.92		
	6235.8	$A_5B_6 + 2CH_3OH$	6259.02 ($n_{1-5} = 23$)	32.18	39.25	
	8331	A_6B_7	7135.19 ($n_{1-6} = 22$)		12.28	
		$A_7B_8 + 2CH_3OH$	8359.19 ($n_{1-7} = 22$)	17.82	32.28	
		A_8B_9	9455.53 ($n_{1-8} = 22$)		16.19	
PCD	113.2	A	116 ($n = 0$)	7.06		1.69
530	173.8			8.46		
	242.0	A	220 ($n = 1$)	8.98		
	315.2	A	334 ($n = 2$)	9.04		
	392.2			8.81		
	473.7	A	471 ($n = 3$)	8.49		
	558.8	A	585 ($n = 4$)	8.08		
	647.7	A	699 ($n = 5$)	7.52		
	740.7			6.90		
	838.9	A	813 ($n = 6$)	6.27		
	944.2	A	927 ($n = 7$)	5.57		
	1058.1	A	1041 ($n = 8$)	4.76		
	1181.7	A	1155 ($n = 9$)	3.79		

Table 2 (*continued*)

Symbol of oligomer	M_n as per MWD curves	Compound	Theoretical molecular weight (g/mol)	Amount of component as calculated by standardisation of GPC chromatograms (wt%)	Amount of component as calculated from reaction mass balance (wt%)	$PD = \bar{M}_w/\bar{M}_n$
	1317.2	A	1383 ($n = 11$)	2.79		
	1466.8	A	1497 ($n = 12$)	1.87		
	1635.4	A	1611 ($n = 13$)	1.09		
	1834.0	A	1725 ($n = 14$)	0.52		
I-530b	397.8	B_2	412	7.94		1.22
	548.5	$A_1B_2 + 2CH_3OH$	541.34 ($n_1 = 0$)	8.92	95.35	
	750.0	$A_1B_2 + 2CH_3OH$	769.34 ($n_1 = 2$)	14.40		
	882.5	$A_1B_2 + 2CH_3OH$	883.34 ($n_1 = 3$)	10.11		
	1014.9	$A_1B_2 + 2CH_3OH$	997.34 ($n_1 = 4$)	8.95		
	1135.4	$A_1B_2 + 2CH_3OH$	1111.34 ($n_1 = 5$)	8.14		
	1263.4	$A_1B_2 + 2CH_3OH$	1225.34 ($n_1 = 6$)	7.29		
	1404.8	$A_1B_2 + 2CH_3OH$	1453.34 ($n_1 = 8$)	6.75		
	1562.6	$A_1B_2 + 2CH_3OH$	1569.34 ($n_1 = 9$)	6.29		
	1736.7	$A_1B_2 + 2CH_3OH$	1795.34 ($n_1 = 11$)	5.78		
	1921.1	$A_1B_2 + 2CH_3OH$	1909.34 ($n_1 = 12$)	5.04		
	2161.8	$A_1B_2 + 2CH_3OH$	2137.34 ($n_1 = 14$)	4.16		
	2421.2	$A_2B_3 + 2CH_3OH$	2490.51 ($n_{1,2} = 11$)	3.14	4.65	
	2695.2	$A_2B_3 + 2CH_3OH$	2718.51 ($n_{1,2} = 13$)	2.04		
	2994.0	$A_2B_3 + 2CH_3OH$	2946.51 ($n_{1,2} = 15$)	1.04		
II-530b	1937.4	A_3B_2	1875.34 ($n_{1,2} = 3$, $n_3 = 4$)	100	90.44	1.83
		A_4B_3	2862.51 ($n_{1-4} = 4$)		9.56	
III-530b	1219.4	$A_1B_2 + 2CH_3OH$	1225.34 ($n_1 = 6$)	16.49		1.61
	2287.1	$A_3B_4 + 2CH_3OH$	2223.68 ($n_{1,2} = 3$, $n_3 = 4$)	41.64	70.45	
		A_4B_5	3210.85 ($n_{1-4} = 4$)		6.69	
	3837.5	$A_5B_6 + 2CH_3OH$	3856.02 ($n_1 = 3$, $n_{2-5} = 4$)	41.87	22.86	
IV-530b	1247.3	A_2B_1	1230.17 ($n_1 = 3$, $n_2 = 4$)	10.42		1.26
	2036.6	A_3B_2	1989.34 ($n_1 = 3$, $n_{2,3} = 4$)	17.71		
	3323.0	A_5B_4	3279.68 ($n_{1-3} = 3$, $n_{4,5} = 4$)	36.01	71.88	
	4213.9	A_6B_5	4152.85 ($n_{1,2} = 3$, $n_{3-6} = 4$)	35.87	6.32	
		A_7B_6	5140.02 ($n_{1-7} = 4$)		21.81	
V-530b	2376.3	$A_3B_4 + 2CH_3OH$	2337.68 ($n_1 = 3$, $n_{2,3} = 4$)	21.76		1.12
	3777.1	$A_5B_6 + 2CH_3OH$	3742.02 ($n_{1,2} = 3$, $n_{3-6} = 4$)	52.92	15.58	
	4553.7	$A_6B_7 + 2CH_3OH$	4501.19 ($n_{1,2} = 3$, $n_{3-6} = 4$)	25.32	1.35	
		A_7B_8	5488.36 ($n_{1-7} = 4$)		4.65	
		A_8B_9	6247.53 ($n_{1-8} = 4$)		78.42	
PCD 1250	1414.5	A	1383 ($n = 11$)	100		1.20
I-1250b	2049.4	$A_1B_2 + 2CH_3OH$	2004.34 ($n_1 = 14$)	100	95.14	1.73
		A_2B_3	3288.51 ($n_{1,2} = 11$)		4.86	
II-1250b	1639.7	A	1611 ($n = 13$)	9.25		1.26

(*continued on next page*)

Table 2 (*continued*)

Symbol of oligomer	M_n as per MWD curves	Compound	Theoretical molecular weight (g/mol)	Amount of component as calculated by standardisation of GPC chromatograms (wt%)	Amount of component as calculated from reaction mass balance (wt%)	$PD = \bar{M}_w/\bar{M}_n$
	2452.8	A_2B_1	2484.17 ($n_{1,2} = 9$)	11.79		
	3382.6	A_2B_1	3396.17 ($n_{1,2} = 13$)	16.73		
	4440.4	A_3B_2	4497.11 ($n_{1-3} = 11$)	33.55	96.52	
	5714.4	A_4B_3	5712.51 ($n_{1-3} = 10$, $n_4 = 11$)	28.66	3.48	
III-1250b	4685.1	$A_3B_4 + 2CH_3OH$	4617.68 ($n_{1,2} = 10$, $n_3 = 11$)	41.71	95.29	1.51
	6601.2	$A_4B_5 + 2CH_3OH$	6630,85 ($n_{1,2} = 11$, $n_{3,4} = 12$)	58.29	3.37	
		A_5B_6	7960.02 ($n_{1-5} = 11$)		1.34	
IV-1250b	3582.9	A_2B_1	3510.17 ($n_1 = 13$, $n_2 = 14$)	5.99		1.11
	4675.0	A_3B_2	4611.34 ($n_{1,2} = 11$, $n_3 = 12$)	9.56		
	5883.3	A_4B_3	5826.51 ($n_{1,2} = 10$, $n_{3,4} = 11$)	14.37		
	7225.0	A_5B_4	7155.68 ($n_{1-4} = 10$, $n_5 = 11$)	24.93	96.60	
	8716.8	A_6B_5	8712.85 ($n_{1-4} = 10$, $n_{5,6} = 11$)	45.14	3.12	
		A_7B_6	10726.02 ($n_{1-7} = 11$)		0.28	
V-1250b	3173.3	$A_2B_3 + 2CH_3OH$	3174.51 ($n_1 = 10$, $n_2 = 11$)	4.56		1.17
	4047.9	$A_3B_4 + 2CH_3OH$	4047.68 ($n_1 = 8$, $n_{2,3} = 9$)	9.31		
	6296.4	$A_4B_5 + 2CH_3OH$	6288,85 ($n_1 = 10$, $n_{2-4} = 11$)	16.06		
	8308.3	$A_5B_6 + 2CH_3OH$	8302.02 ($n_{1,2} = 11$, $n_{3-5} = 12$)	34.12	79.66	
	9552.2	$A_6B_7 + 2CH_3OH$	9517.19 ($n_{1-6} = 11$)	35.99	2.56	
		A_7B_8	11074.36 ($n_{1-7} = 11$)		0.23	
		A_8B_9	12631.53 ($n_{1-8} = 11$)		17.56	

[a] Designations: (1) n_i ($i = 2-14$)—theoritically calculated polymerisation degree (DP) in POG or PCD; (2) $A_nB_{n+1} + 2CH_3OH$—provides the information that the saved file corresponds to the isocyanate prepolymer A_nB_{n+1} which has been blocked on both sides with methanol (when samples were being prepared for analysis)

non-linear chromatography (NLC) functions to curves after their deconvolution. The obtained results are presented in Table 2.

4. Discussion of results

It was very important for the suggested method that the polyurethane mixture had to be purified carefully, i.e. unreacted diisocyanate and polyol monomers had to be removed therefrom. That can be accomplished by conservative evaporation in vacuum evaporators, what is not so frequently employed in practice, or by means of selective extraction [20]. The latter method was adopted for our work. It was necessary to find selective extraction solvents for every stage of the step-by-step polyaddition process, both for TDI and for hydroxyl monomers. Different polarity specifications of BD, POG and PCD had to be taken into consideration for that process [13].

Extraction was continued until the content of –NCO groups was obtained which conformed to that calculated theoretically. Fig. 4 shows diagrams for determined concentrations of –NCO groups in synthesised isocyanate products before and after extraction. The experimental values can be seen close to those calculated from the material balance—excess TDI must have been completely washed away from the products in practice. The presence of unconverted monomers was found to have a strong impact on viscosity of products obtained at successive stages of the polymerisation process: those monomers were masking essential changes in actual viscosities of products which were caused both by the use of polyols with higher and higher molecular weights, and by the increasing molecular weight of oligourethanes.

It is apparent from Fig. 5 that the effects of those factors can be observed only after monomers have been separated. Viscosity figures for oligourethanes with –OH terminal groups were found to be higher than those for their isocyanate-terminated analogues and they generally become smaller when polyols used for the reaction have higher molecular weights. The IR spectra confirmed the expected structures of the obtained products.

As results from the examples of IR spectra (Figs. 6 and 7), the structures of oligomers obtained from the same polyols at odd stages (isocyanate prepolymers) and at even stages (urethane–hydroxyl prepolymers) were—as expected—very much similar within individual groups of compounds. Hence, the most essential differences should result solely from the sizes of molecules of individual oligomers. The band at about 2272 cm^{-1} which represents asymmetrical stretching vibrations of –NCO groups is the most specific band for isocyanates and it can be observed in case of isocyanate oligomers A_nB_{n+1} only. On the other hand, the band for stretching vibrations of –OH groups at 3450 cm^{-1} appears only in spectra obtained for hydroxyl oligomers $A_{n+1}B_n$. When the molecular weight of an oligomer increases, absorption intensity decreases for both these bands, while higher intensities are observed for the amide I band (at 1730 cm^{-1}) and amide II band (at 1536 cm^{-1}). The former is shifted towards lower frequency values which proves the presence of hydrogen bonds, and the latter represents the combination of scissoring vibrations in –N–H and stretching vibrations in –C–N groups [21, 22].

No band was found at 2130 cm^{-1} in IR spectra which

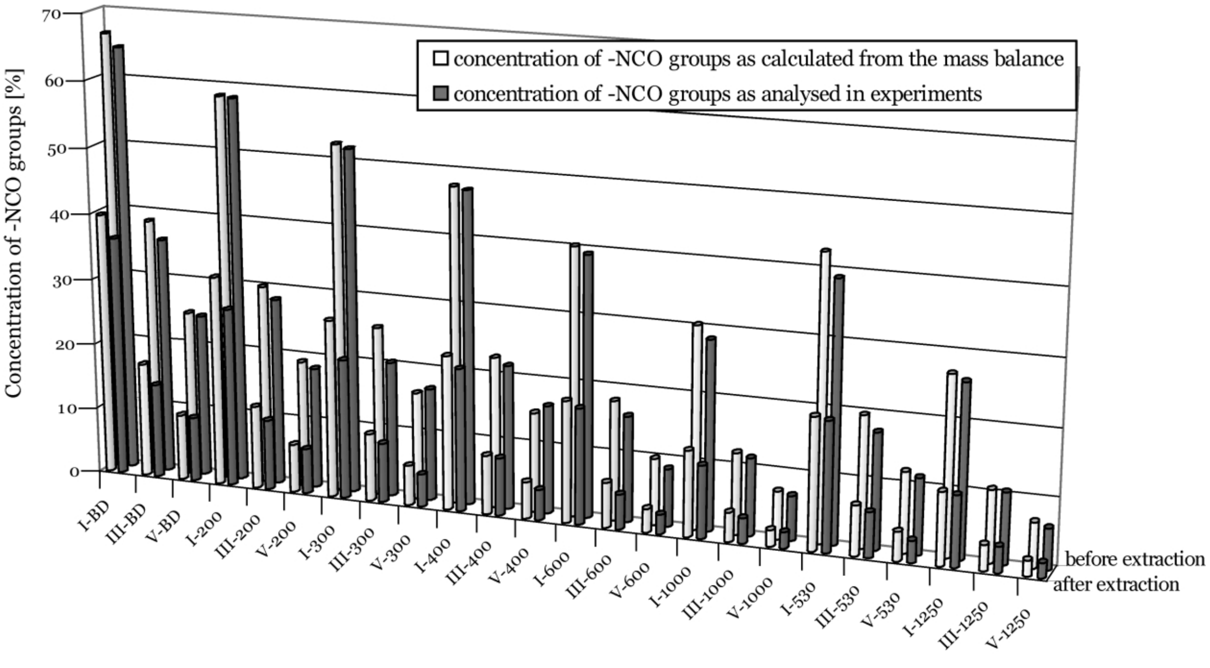

Fig. 4. Determined concentrations of free –NCO groups in prepolymers against the values calculated from mass balances.

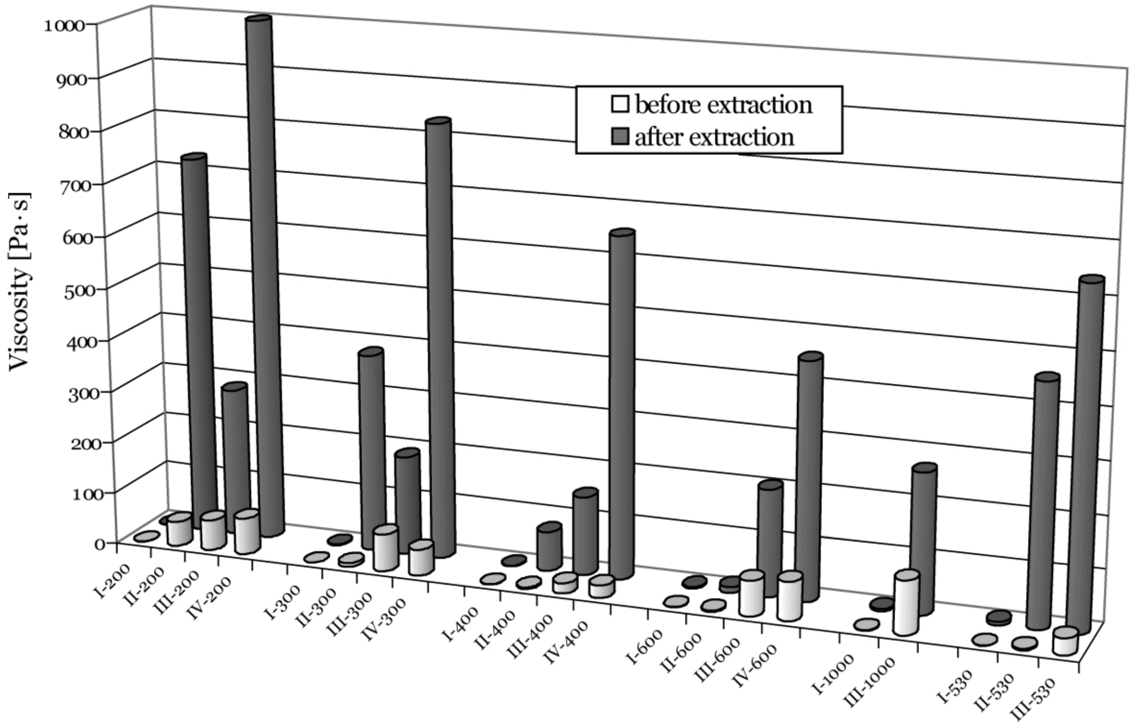

Fig. 5. Viscosities of obtained urethane oligomers before and after extraction.

could represent carbodiimides, and a wide band was observed at 1695–1755 cm^{-1} (max. at 1725–1730 cm^{-1}) which in theory could represent urethidiones formed during dimerisation of isocyanates. On the other hand, the band at 1410 cm^{-1}, which is attributed to isocyanurates, appears in some spectra only and its signal is not very high. Thus, one can infer that only some small amount of excess isocyanates has been converted to undesirable by-products. That is essential for the concept of the whole study as it confirms that the conditions adopted for the synthesis have made it possible to obtain generally linear urethane oligomers with –NCO terminal groups, even at a relatively high excess of the isocyanate monomer [23].

Confirmation of chemical structures of urethane oligomer chains (Table 2) made the first step towards learning complete compositions of synthesised polymers. Following the idea of scheme (2), PUs obtained at successive stages of the polyaddition process should be initially mixtures of monomers and oligomers, and after extraction—mixtures of predominantly oligourethanes, and it is necessary to identify individual components. This problem was solved by analysing individual samples with the use of gel permeation chromatography (GPC) as well as mass spectrometry (ESI and MALDI-TOF) methods in which mild excitation techniques were employed to take records of basic

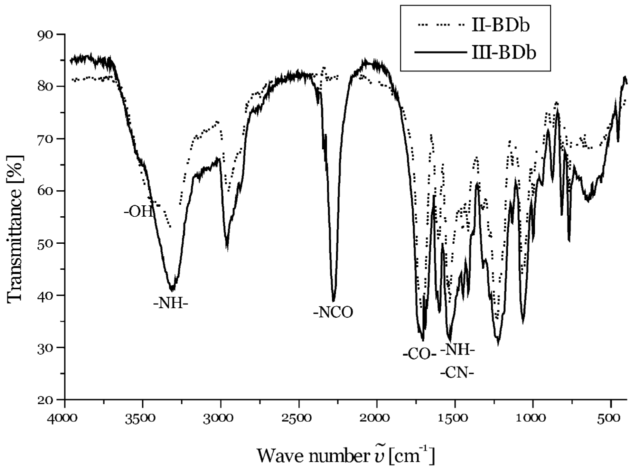

Fig. 6. IR spectra of isocyanate oligomer and hydroxyl oligomer obtained from the second and third stages of the reaction of 1,4-butanediol and TDI (II-BD b and III-BD b as per Table 1).

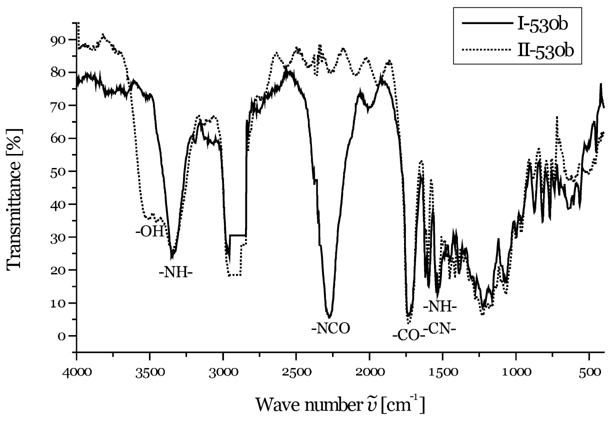

Fig. 7. IR spectra of isocyanate oligomer and hydroxyl oligomer obtained from the first and second stages of the reaction of PCD-530 and TDI (I-530 and II-530 as per Table 1).

molecular ions. It was possible from GPC chromatograms which were recorded with the use of three detectors: RI, LS and DV, to obtain a reasonably precise function of molecular weight distribution (MWD) for individual samples of studied oligomers and to make their quantitative evaluation (Table 2).

The obtained data were correlated with the figures calculated from the mass balance for individual steps in the synthesis. It is obvious that the basic reason for polydispersity of every urethane oligomer sample is primarily polydispersity of the hydroxyl component itself. All diols, except for BD, were inhomogeneous materials as regards their chemical compositions. Hence, adequate polymerisation degrees n_i were required to be attributed to every component (i.e. to every peak) in chromatograms of POG or PCD. Then, in order to be able to compare homogeneity features of oligourethanes produced at successive polyaddition stages, the Peak Fit v4. software was employed to calculate the corresponding MWD curves. The exemplary charts are shown in Figs. 8–10.

The adopted procedure made it possible to observe the step-by-step growth of molecular weights of oligomers produced at every step of polymerisation. The best chromatographic separation was obtained for samples taken from the reactor just after step 1 and step 2, when the chemical composition of the mixture analysed was reasonably simple. Good separation was then harder and harder to achieve as the mean molecular weights of products increased. The obtained MWD curves—especially for stage 5 and stage 6—became similar to those described in reports for high-molecular-weight PUs synthesised for example of ethylene glycol polyadipate, TDI or MDI and then expanded with ethylene glycol [24].

One dominant oligourethane is usually observed in the polymer mixtures after the first two stages; its structure results from adopted stoichiometry (Table 1). The chemical compositions of products obtained from further stages become much more complex and adopted stoichiometry is decisive more for the types of terminal functional groups rather than for reaction selectivity. In parallel to the most welcome oligomer, there are always a few other products present and their shares happen to be comparable to that of the required product. Some small amounts of high-molecular-weight products appear as early as at the initial two steps. For example, step 1 will yield A_1B_2 but also isocyanate oligourethanes with higher molecular weights (A_2B_3 and A_3B_4) will be produced. Unconverted monomers can also be observed in some samples.

Further polymerisation steps produce compounds with higher molecular weights, as expected, but they also yield lower oligomers, probably by the reaction of monomers introduced with monomers which have not been completely removed from previously synthesised products.

The recorded chromatograms made the basis for the calculations of number average ($\bar{M}_n$) and weight average ($\bar{M}_w$) molecular weights as well as polydispersity degrees $PD = \bar{M}_w/\bar{M}_n$ for the products formed. The values for the latter fall within 1.05–2.37 and they tend to be even closer to the scope of 1.1–1.3. No distinct increase in the scatter of molecular weights could be observed along the sequence of polyaddition stages—that is advantageous for the process offered. The values of $PD > 1.3$ are specific for oligourethanes in which some amounts of monomers can be found after they have not been extracted out completely, and in particular for isocyanate prepolymers in which some small amounts of TDI are present.

The ESI and MALDI-TOF mass spectrometry methods were employed to unambiguously identify individual compounds within the analysed samples which had been found present on the basis of GPC analyses. The bands are visible in recorded MS spectra which can be attributed to the suggested molecular ions of oligomers, i.e. their sizes and structures, with the atomic weights of Na^+, K^+ or H^+ cations added, as results from the adopted excitation method. Majority of positive ions present in ESI spectra contain K which has been introduced as KI, and some minor

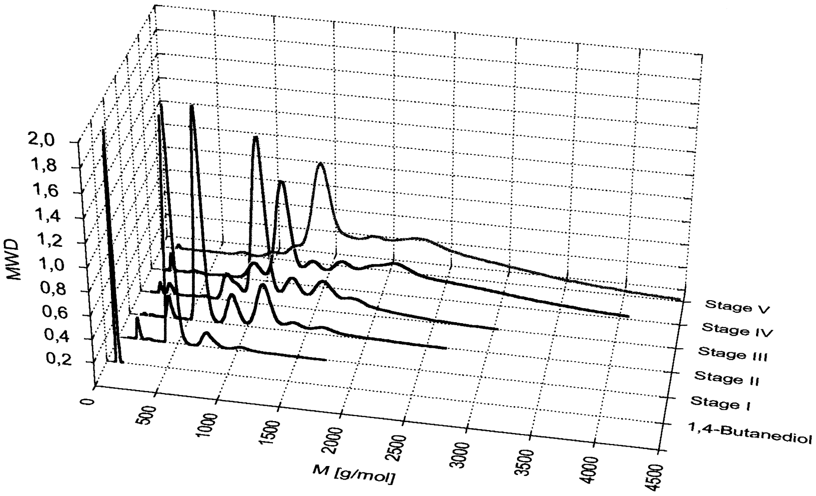

Fig. 8. MWD curves for oligomers (I–V) BDb (Table 2).

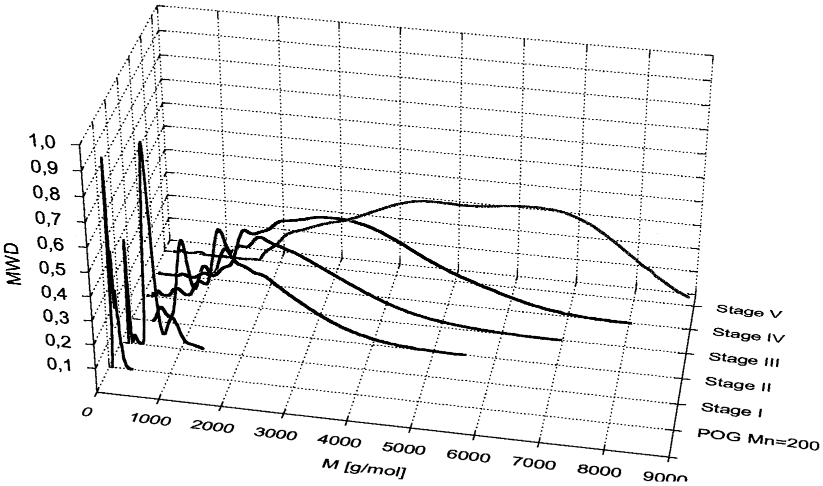

Fig. 9. MWD curves for oligomers (I–V) 200b (Table 2).

part of them contain Na. MALDI-TOF spectra principally take records of adducts of oligomers and Na^+ or H^+ cations, and also possibly of K^+ (about 15%) [1,2]. Additionally, isocyanate products reacted with methanol employed to dissolve samples which is also apparent in our findings.

The recorded spectra reveal generally a high number of M/z signals with much diversified intensities; after a detailed analysis, we managed to make signal-product pairs for majority of expected adducts. Theoretically calculated molecular weights of polyols and urethane oligomers match with the locations of their corresponding signals in MS spectra. Every spectrum has been made up of a specific sequence of signals arranged at the intervals of $M/z = 44$ from each other, that corresponds to the structural unit of $-CH_2CH_2O-$ for POG, or at the intervals of $M/z = 114$ (i.e. $-CO(CH_2)_5O-$) for PCD (Table 3).

The ESI spectra can take records of MWD only up to the value of $M/z = 1200$. Hence, it was impossible to fully identify the components of the samples studied (Figs. 11 and 12) [25,26]. Additional information on the chemical compositions of the investigated oligomers could be obtained by comparing ESI spectra to GPC findings.

The MALDI-TOF technique is capable of analysing a much broader scope of M/z. Just for illustration, Figs. 13 and 14 show exemplary spectra for oligomers obtained from two stages of reactions of TDI and POG 300, while the detailed interpretation of spectra for all the synthesised oligomers have been shown in Table 3.

The employed MS methods complement the chemical compositions of oligomers as found by GPC and make them reliable. Said compositions are much more complex than one could expect from the balance calculations and from kinetic modelling, still the general compatibility with the model has been kept. In the MS spectra recorded, signals can be seen, which represent, for example, oligourethanes created from POG or PCD molecules with various polymerisation degrees n_i. When individual molecular ions are precisely recorded with the use of MALDI-TOF technique, the compounds, which could not be isolated with the GPC method due to poor separation of individual

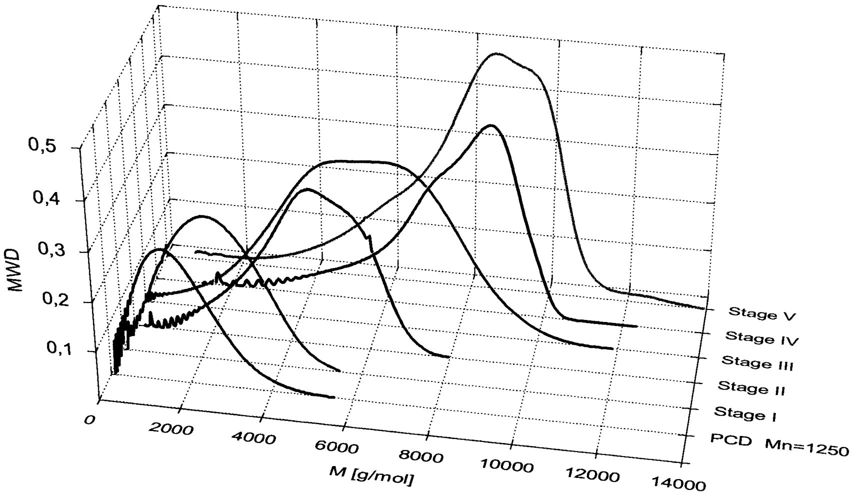

Fig. 10. MWD curves for oligomers (I–V) 1250b (Table 2).

Table 3
Interpretation for mass spectra of urethane oligomers

Designations for oligomers as per Table 1	Type of MS method	No. of fig.	Band location (*M*/*z*)	Relative intensity (%)	Probable structure of molecular ion	Calculated molecular weight (g/mol)
I-BDb	MALDI		525	100	$A_1B_2 + Na^+ + 2CH_3OH$	523.34
			675	5.71	$A_3B_2 + Na^+ + CH_3OH$	673.34
			790	2.86	$A_2B_3 + Na^+ + 2CH_3OH$	789.51
II-BDb	MALDI		378	22.22	$A_2B_1 + Na^+$	377.17
			642	100	$A_3B_2 + Na^+$	641.34
			792	5.19	$A_3B_3 + H^+$	793.51
			907	2.22	$A_4B_3 + Na^+$	906.51
			1171	1.11	$A_5B_4 + Na^+$	1170.68
III-BDb	MALDI		261	46.15	$B + Na^+ + 2CH_3OH$	261.17
			525	18.27	$A_1B_2 + Na^+ + 2CH_3OH$	523.34
			551	34.61	$A_2B_2 + Na^+$	551.34
			790	20.19	$A_2B_3 + Na^+ + 2CH_3OH$	789.51
			1054	100	$A_3B_4 + Na^+ + 2CH_3OH$	1053.68
			1203	8.65	$A_4B_4 + 2CH_3OH$	1204.68
			1319	6.73	$A_4B_5 + Na^+ + 2CH_3OH$	1317.85
			1583	7.70	$A_5B_6 + Na^+ + 2CH_3OH$	1582.02
			1848	1.92	$A_6B_7 + Na^+ + 2CH_3OH$	1846.19
IV-BDb	MALDI		361	47.28	$A_2B_1 + H^+$	355.17
			551	29.09	$A_2B_2 + Na^+$	551.34
			906	18.17	$A_4B_3 + Na^+$	906.51
			1171	100	$A_5B_4 + Na^+$	1170.68
			1320	9.10	$A_5B_5 + H^+$	1321.85
			1435	7.28	$A_6B_5 + Na^+$	1433.85
V-BDb	MALDI		262	97.83	$B + Na^+ + 2CH_3OH$	261.17
			376	84.79	$B_2 + Na^+$	371.34
			414	100	$B_2 + H^+ + 2CH_3OH$	413.34
			525	35.87	$A_1B_2 + Na^+ + 2CH_3OH$	523.34
			551	73.92	$A_2B_2 + Na^+$	551.34
			995	11.96	$A_3B_4 + H^+ + CH_3OH$	999.68
			1201	14.14	$A_4B_4 + H^+ + 2CH_3OH$	1205.68
			1583	32.60	$A_5B_6 + Na^+ + 2CH_3OH$	1582.02
			1848	4.35	$A_6B_7 + Na^+ + 2CH_3OH$	1846.19
			1938	2.17	$A_7B_7 + Na^+ + 2CH_3OH$	1936.19
			2112	3.27	$A_7B_8 + Na^+ + 2CH_3OH$	2110.36
			2641	3.27	$A_9B_{10} + Na^+ + 2CH_3OH$ H	2638.70
POG 200	ESI		409.1	100	$A + K^+$	409 ($n = 8$)
			365.1	88.00	$A + K^+$	365 ($n = 7$)
I-200b	ESI	11	689.2	100	$A_1B_2 + Na^+$	692.34 ($n_1 = 6$)

(*continued on next page*)

Table 3 (*continued*)

Designations for oligomers as per Table 1	Type of MS method	No. of fig.	Band location (*M*/*z*)	Relative intensity (%)	Probable structure of molecular ion	Calculated molecular weight (g/mol)
II-200b	ESI	12	365.1	100	$A + K^+$	365 ($n = 7$)
			969.3	97.00	$A_3B_2 + K^+$	969.34 ($n_{1-3} = 4$)
			1013.4	100	$A_3B_2 + K^+$	1013.34 ($n_{1,2} = 4, n_3 = 5$)
	MALDI		542	48.25	$A_2B_1 + Na^+$	541.17 ($n_1 = 3, n_2 = 4$)
			954	100	$A_3B_2 + Na^+$	953.34 ($n_{1-3} = 4$)
			1279	30.07	$A_4B_3 + Na^+$	1277.51 ($n_1 = 3, n_{2-4} = 4$)
			1647	20.98	$A_5B_4 + Na^+$	1645.68 ($n_1 = 3, n_{2-5} = 4$)
			2060	7.69	$A_6B_5 + Na^+$	2057.85 ($n_{1-6} = 4$)
			2428	3.50	$A_7B_6 + Na^+$	2426.02 ($n_{1-7} = 4$)
III-200b	ESI		689.2	100	$A_1B_2 + Na^+$	692.34 ($n_1 = 6$)
	MALDI		610	100	$A_1B_2 + Na^+$	609.34 ($n_1 = 5$)
			935	48.91	$A_2B_3 + Na^+$	933.51 ($n_{1,2} = 4$)
			1259	92.39	$A_3B_4 + Na^+$	1257.68 ($n_1 = 3, n_{2,3} = 4$)
			1628	31.52	$A_4B_5 + Na^+$	1625.85 ($n_1 = 3, n_{2-4} = 4$)
			1996	20.65	$A_5B_6 + Na^+$	1994.02 ($n_1 = 3, n_{2-5} = 4$)
			2409	7.61	$A_6B_7 + Na^+$	2406.19 ($n_{1-6} = 4$)
IV-200b	ESI		365.1	100	$A + K^+$	365 ($n = 7$)
			645.2	38	$A_2B_1 + K^+$	645.17 ($n_1 = 4, n_2 = 5$)
			969	35	$A_3B_2 + K^+$	969.34 ($n_{1-3} = 4$)
	MALDI		586	39.00	$A_2B_1 + Na^+$	585.17 ($n_{1,2} = 4$)
			955	36.00	$A_3B_2 + Na^+$	953.34 ($n_{1-3} = 4$)
			1279	36.00	$A_4B_3 + Na^+$	1277.51 ($n_1 = 3, n_{2-4} = 4$)
			1692	100	$A_5B_4 + Na^+$	1689.68 ($n_{1-5} = 4$)
			2060	52.00	$A_6B_5 + Na^+$	2057.85 ($n_{1-6} = 4$)
			2385	43.00	$A_7B_6 + Na^+$	2382.02 ($n_1 = 3, n_{2-7} = 4$)
			2797	22.00	$A_8B_7 + Na^+$	2794.19 ($n_{1-8} = 4$)
			3077	17.21	$A_9B_8 + Na^+$	3074.36 ($n_{1,2} = 3, n_{3-9} = 4$)
			3490	10.4	$A_{10}B_9 + Na^+$	3486.53 ($n_1 = 3, n_{2-10} = 4$)
			3814	7.17	$A_{11}B_{10} + Na^+$	3810.70 ($n_{1,2} = 3, n_{3-11} = 4$)
V-200b	ESI		689.2	94	$A_1B_2 + Na^+$	692.34 ($n_1 = 6$)
			733.2	100	$A_1B_2 + Na^+$	736.34 ($n_1 = 7$)
	MALDI		1129	100	$A_2B_3 + Na^+ + 2CH_3OH$	1129.51 ($n_1 = 5, n_2 = 6$)
			1260	86.57	$A_3B_4 + Na^+$	1257.68 ($n_1 = 3, n_{2,3} = 4$)
			1454	91.04	$A_3B_4 + H^+$	1455.68 ($n_1 = 5, n_2 = 6$)
			1630	95.52	$A_4B_5 + Na^+$	1625.85 ($n_1 = 3, n_{2-4} = 4$)
			1998	91.79	$A_5B_6 + Na^+$	1994.02 ($n_1 = 3, n_{2-5} = 4$)
			2411	39.55	$A_6B_7 + Na^+$	2406.19 ($n_{1-6} = 4$)
I-300b	MALDI	13	718	100	$A_1B_2 + Na^+ + 2CH_3OH$	717.34 ($n_1 = 6$)
			1218	11.84	$A_2B_3 + Na^+ + 2CH_3OH$	1217.51 ($n_1 = 6, n_2 = 7$)
II-300b	MALDI		938	7.25	$A_2B_1 + Na^+$	937.17 ($n_{1,2} = 8$)
			1262	100	$A_3B_2 + Na^+$	1261.34 ($n_{1,2} = 6, n_3 = 7$)
			1630	13.58	$A_4B_3 + Na^+$	1629.68 ($n_1 = 5, n_{2-4} = 6$)
			2130	20.99	$A_5B_4 + Na^+$	2129.68 ($n_{1-5} = 6$)

Table 3 (*continued*)

Designations for oligomers as per Table 1	Type of MS method	No. of fig.	Band location (M/z)	Relative intensity (%)	Probable structure of molecular ion	Calculated molecular weight (g/mol)
III-300b	MALDI		1061	43.90	$A_2B_3 + H^+ + 2CH_3OH$	1063.51 ($n_{1,2} = 5$)
			1630	100	$A_3B_4 + H^+$	1631.68 ($n_1 = 6, n_{2,3} = 7$)
			2086	14.63	$A_4B_5 + H^+$	2087.85 ($n_{1,2} = 6, n_{3,4} = 7$)
			2498	13.41	$A_5B_6 + H^+$	2500.02 ($n_{1-4} = 6, n_5 = 7$)
IV-300b	MALDI		1210	78.16	$A_3B_2 + Na^+$	1217.51 ($n_{1-3} = 6$)
			1675	32.18	$A_4B_3 + Na^+$	1673.68 ($n_{1-4} = 6$)
			2132	100	$A_5B_4 + Na^+$	2129.68 ($n_{1-5} = 6$)
			3001	28.74	$A_6B_5 + H^+$	3003.85 ($n_{1,2} = 7, n_{3-6} = 8$)
			3546	10.34	$A_7B_6 + H^+$	3548.02 ($n_{1,2} = 7, n_{3-7} = 8$)
			3959	9.20	$A_8B_7 + H^+$	3960.19 ($n_{1-5} = 7, n_{6-8} = 8$)
V-300b	MALDI	14	1599	41.46	$A_3B_4 + Na^+ + CH_3OH$	1597.68 ($n_{1-3} = 6$)
			2190	47.56	$A_4B_5 + H^+ + 2CH_3OH$	2195.85 ($n_1 = 6, n_{2-4} = 7$)
			2544	100	$A_5B_6 + H^+$	2544.02 ($n_{1-3} = 6, n_{4,5} = 7$)
			2956	32.93	$A_6B_7 + H^+$	2956.19 ($n_{1-5} = 6, n_6 = 7$)
			3368	39.02	$A_7B_8 + H^+$	3368.36 ($n_{1-7} = 6$)
			3957	13.41	$A_8B_9 + H^+$	3956.53 ($n_{1-5} = 6, n_{6-8} = 7$)
			4369	9.76	$A_9B_{10} + H^+$	4368.7 ($n_{1-7} = 6, n_{8,9} = 7$)
POG 400	ESI		497.2	100	$A + K^+$	497 ($n = 10$)
I-400b	ESI		849.3	100	A_1B_2	850 ($n_1 = 11$)
II-400b	ESI		497.2	100	$A + K^+$	497 ($n = 10$)
	MALDI		350	100	$A + Na^+$	349 ($n = 7$)
			911	8.66	$A_2B_1 + H^+$	915.17 ($n_{1,2} = 8$)
			1483	12.70	$A_3B_2 + Na^+$	1481.34 ($n_{1-3} = 8$)
			2028	1.54	$A_4B_3 + Na^+$	2025.51 ($n_{1-4} = 8$)
			2529	1.00	$A_5B_4 + Na^+$	2525.68 ($n_1 = 7, n_{2-5} = 8$)
III-400b	ESI		849.1	100	A_1B_2	850 ($n_1 = 11$)
	MALDI		742	100	$A_1B_2 + 2CH_3OH$	738.34 ($n_1 = 7$)
			1288	13.38	$A_2B_3 + Na^+$	1285.51 ($n_{1,2} = 8$)
			1832	28.17	$A_3B_4 + Na^+$	1829.68 ($n_{1-3} = 8$)
			2289	5.63	$A_4B_5 + Na^+$	2285.85 ($n_{1,2} = 7, n_{3,4} = 8$)
			2657	4.93	$A_5B_6 + Na^+$	2654.02 ($n_1 = 6, n_{2-5} = 7$)
IV-400b	ESI		497.2	100	$A + K^+$	497 ($n = 10$)
	MALDI		350	100	$A + Na^+$	349 ($n = 7$)
			851	8.06	$A_2B_1 + Na^+$	849.17 ($n_{1,2} = 7$)
			1102	3.23	$A_2B_2 + H^+$	1100.34 ($n_1 = 7, n_2 = 8$)
			1527	3.23	$A_3B_2 + Na^+$	1525.34 ($n_{1,2} = 8, n_3 = 9$)
			2528	1.95	$A_5B_4 + Na^+$	2525.68 ($n_1 = 7, n_{2-5} = 8$)
			3161	0.65	$A_6B_5 + Na^+$	3157.85 ($n_1 = 7, n_{2-6} = 8$)
			3661	0.43	$A_7B_6 + Na^+$	3658.02 ($n_{1-7} = 8$)
V-400b	ESI		583.2	100	$A_1B_1 + K^+$	583.17 ($n_1 = 8$)

(*continued on next page*)

Table 3 (*continued*)

Designations for oligomers as per Table 1	Type of MS method	No. of fig.	Band location (M/z)	Relative intensity (%)	Probable structure of molecular ion	Calculated molecular weight (g/mol)
			627.1	73	$A_1B_1 + K^+$	627.17 ($n_1 = 9$)
	MALDI		903	100	$A_2B_2 + H^+ + CH_3OH$	901.34 ($n_1 = 5, n_2 = 6$)
			1053	57.33	$A_2B_2 + Na^+ + CH_3OH$	1055.34 ($n_{1,2} = 7$)
			1227	28.67	$A_2B_3 + Na^+ + CH_3OH$	1229.51 ($n_{1,2} = 7$)
			1413	21.42	$A_3B_3 + H^+$	1413.51 ($n_{1,2} = 6, n_3 = 7$)
			1627	14.33	$A_3B_4 + H^+$	1631.68 ($n_{1,2} = 6, n_3 = 7$)
			1953	7.08	$A_4B_5 + H^+$	1955.85 ($n_1 = 5, n_{2-4} = 6$)
			2629	5.11	$A_5B_6 + H^+$	2632.02 ($n_1 = 6, n_{2-5} = 7$)
			3040	3.26	$A_6B_7 + H^+$	3044.19 ($n_{1-3} = 6, n_{4-6} = 7$)
POG 600	MALDI		614	100	$A + Na^+$	613 ($n = 13$)
I-600b	MALDI		875	100	$A_1B_2 + Na^+$	873.34 ($n_1 = 11$)
II-600b	MALDI		570	100	$A + Na^+$	569 ($n = 12$)
			1335	7.80	$A_2B_1 + Na^+$	1337.17 ($n_1 = 12, n_2 = 13$)
			2143	46.10	$A_3B_2 + Na^+$	2141.34 ($n_{1-3} = 13$)
			2820	6.40	$A_4B_3 + Na^+$	2817.51 ($n_{1,2} = 12, n_{3,4} = 13$)
			3628	6.30	$A_5B_4 + Na^+$	3625.68 ($n_1 = 12, n_{2-5} = 13$)
III-600b	MALDI		1027	100	$A_1B_2 + H^+$	1027.34 ($n_1 = 11$)
			1793	11.97	$A_2B_3 + H^+$	1791.51 ($n_{1,2} = 14$)
			2556	33.80	$A_3B_4 + H^+$	2555.68 ($n_1 = 13, n_{2,3} = 14$)
			3337	4.93	$A_4B_5 + H^+ + CH_3OH$	3339.51 ($n_{1-3} = 13, n_4 = 14$)
IV-600b	MALDI		573	57.14	$A + Na^+$	569 ($n = 12$)
			1135	100	$A_2B_1 + H^+$	1135.17 ($n_1 = 10, n_2 = 11$)
			2099	18.00	$A_3B_2 + Na^+$	2097.34 ($n_1 = 12, n_{2,3} = 13$)
			3145	8.67	$A_4B_3 + H^+$	3147.51 ($n_{1,2} = 14, n_{3,4} = 15$)
			3672	4.79	$A_5B_4 + Na^+$	3669.68 ($n_{1-5} = 13$)
			4589	2.43	$A_6B_5 + H^+$	4587.85 ($n_{1,2} = 13, n_{3-6} = 14$)
V-600b	MALDI		1061	100	$A_1B_2 + H^+ + CH_3OH$	1059.34 ($n_1 = 15$)
			2321	17.20	$A_3B_4 + H^+$	2323.68 ($n_1 = 11, n_{2,3} = 12$)
			3249	11.67	$A_4B_5 + H^+ + 2CH_3OH$	3251.85 ($n_1 = 12, n_{2-4} = 13$)
			4043	6.48	$A_5B_6 + H^+$	4040.02 ($n_{1-4} = 13, n_5 = 14$)
			4629	6.05	$A_6B_7 + H^+$	4628.19 ($n_{1-3} = 12, n_{4-6} = 13$)
POG 1000	MALDI		923	100	$A + Na^+$	921 ($n = 20$)
I-1000b	MALDI		1272	100	$A_1B_2 + Na^+$	1269.34 ($n_1 = 20$)
II-1000b	MALDI		923	100	$A + Na^+$	921 ($n = 20$)
			2276	20.2	$A_2B_1 + H^+$	2279.17 ($n_1 = 23, n_2 = 24$)
			3377	28.28	$A_3B_2 + Na^+$	3373.34 ($n_{1,2} = 22, n_3 = 23$)
			4510	5.4	$A_4B_3 + H^+$	4507.85 ($n_{1-3} = 20, n_4 = 21$)
III-1000b	MALDI		1379	100	$A_1B_2 + H^+$	1379.34 ($n_1 = 23$)
			2512	19.12	$A_2B_3 + Na^+$	2514.51 ($n_1 = 21, n_2 = 22$)
			3702	13.24	$A_3B_4 + H^+$	3699.68 ($n_{1,2} = 22, n_3 = 23$)

Table 3 (*continued*)

Designations for oligomers as per Table 1	Type of MS method	No. of fig.	Band location (M/z)	Relative intensity (%)	Probable structure of molecular ion	Calculated molecular weight (g/mol)
			5098	2.94	$A_4B_5 + Na^+$	5101.85 ($n_{1,2} = 23, n_{3,4} = 24$)
IV-1000b	MALDI		922	100	$A + Na^+$	921 ($n = 20$)
			2173	57.31	$A_2B_1 + Na^+$	2169.17 ($n_{1,2} = 22$)
			3349	14.93	$A_3B_2 + H^+$	3351.48 ($n_{1,2} = 22, n_3 = 23$)
			4644	10.40	$A_4B_3 + H^+$	4643.51 ($n_{1-4} = 23$)
			5319	10.11	$A_5B_4 + H^+$	5319.68 ($n_{1,2} = 20, n_{3,4} = 21$)
V-1000b	MALDI		1315	100	$A_1B_2 + Na^+$	1313.17 ($n_1 = 21$)
			2468	20.29	$A_2B_3 + H^+ + 2CH_3OH$	2471.51 ($n_{1,2} = 21$)
			3495	7.25	$A_3B_4 + H^+ + 2CH_3OH$	3499.68 ($n_{1,2} = 20, n_3 = 21$)
			4597	3.93	$A_4B_5 + H^+$	4595.85 ($n_1 = 20, n_{2-4} = 21$)
			5714	2.85	$A_5B_6 + H^+$	5712.02 ($n_1 = 20, n_{2-5} = 21$)
			6681	2.37	$A_6B_7 + H^+ + CH_3OH$	6684.19 ($n_{1-5} = 20, n_6 = 21$)
PCD 530	MALDI		586	100	$A + Na^+$	585 ($n = 4$)
II-530b	MALDI		358	100	$A + Na^+$	357 ($n = 2$)
			1375	14.81	$A_3B_2 + Na^+$	1373.34 ($n_{1-3} = 2$)
III-530b	MALDI		1054	100	$A_1B_2 + H^+ + CH_3OH$	1057.34 ($n_1 = 5$)
			1679	56.00	$A_2B_3 + H^+ + CH_3OH$	1679.51 ($n_{1,2} = 4$)
			2380	10.40	$A_3B_4 + H^+$	2383.68 ($n_{1-3} = 4$)
IV-530b	MALDI		359	100	$A + Na^+$	357 ($n = 2$)
			863	11.11	$A_2B_1 + Na^+$	865.17 ($n_{1,2} = 2$)
			1377	1.47	$A_3B_2 + Na^+$	1373.34 ($n_{1-3} = 2$)
			1878	0.73	$A_4B_3 + Na^+$	1881.51 ($n_{1-4} = 2$)
PCD 1250	MALDI		586	100	$A + Na^+$	585 ($n = 4$)
II-1250b	MALDI		815	100	$A + Na^+$	815 ($n = 6$)
			1894	3.01	$A_2B_1 + Na^+$	1891.17 ($n_1 = 6, n_2 = 7$)
			3201	2.37	$A_3B_2 + Na^+$	3198.34 ($n_{1,2} = 7, n_3 = 8$)
III-1250b	MALDI		995	100	$A_1B_2 + Na^+ + 2CH_3OH$	997.17 ($n_1 = 4$)
			1252	45.00	$A_1B_2 + H^+$	1253.34 ($n_1 = 7$)
			1553	40.00	$A_2B_3 + Na^+$	1555.51 ($n_1 = 3, n_2 = 4$)
IV-1250b	MALDI		1155	100	$A + Na^+$	1155 ($n = 9$)
			3884	0.95	$A_3B_2 + Na^+$	3881.34 ($n_{1,2} = 9, n_3 = 10$)
			4503	0.63	$A_4B_3 + Na^+$	4503.51 ($n_1 = 7, n_{2-4} = 8$)
			5241	0.48	$A_5B_4 + Na^+$	5239.68 ($n_{1-5} = 7$)
V-1250b	MALDI		994	55.56	$A_1B_2 + Na^+ + 2CH_3OH$	997.17 ($n_1 = 4$)
			1201	100	$A_1B_2 + H^+ + 2CH_3OH$	1203.34 ($n_1 = 6$)
			1527	19.44	$A_2B_3 + H^+$	1533.51 ($n_1 = 3, n_2 = 4$)

Designations: (1) n_i—polymerisation degree (DP) in POG or PCD.

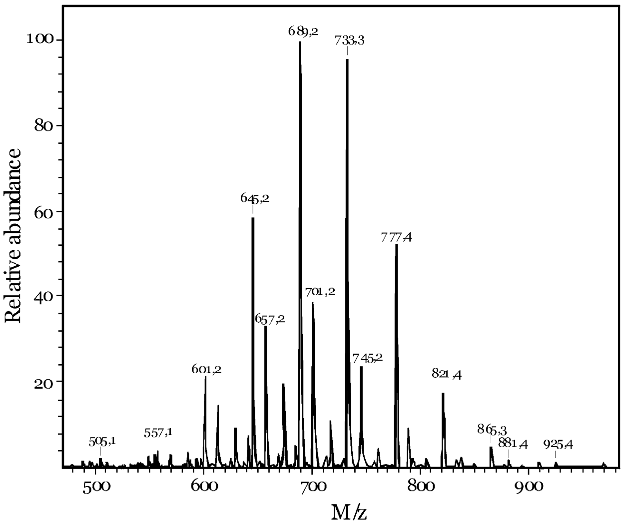

Fig. 11. ESI spectrum for oligourethane I-200b (Table 3).

components, even with the use of three chromatographic columns connected in parallel, can be identified. Some MS spectra reveal the presence of oligomers with the compositions close to expectations, which seemed to be 'missing' in GPC, while some other spectra demonstrate many more high-molecular-weight products which have been recorded in chromatograms in the form of so-called 'tails'.

We also made attempts to correlate the findings from quantitative determinations with the data obtained from mass balances for the reactions (Table 1). It was assumed for the qualitative evaluation of chromatograms that the peak areas were representative for concentrations of the components, and the linear performance profile was also assumed for the RI detector. The values of d*n*/d*c* for monomers are in fact lower than those for oligomers, and hence the concentrations calculated for the former could be overestimated [27,28]. Deviations from d*n*/d*c* for oligomers higher than tetramers were assumed to be negligible and thus the detector signals to be proportional to concentrations. Deconvolution of poorly separated peaks was necessary for quantitative measurements by the internal standardization method, what was possible with the use of the computer software.

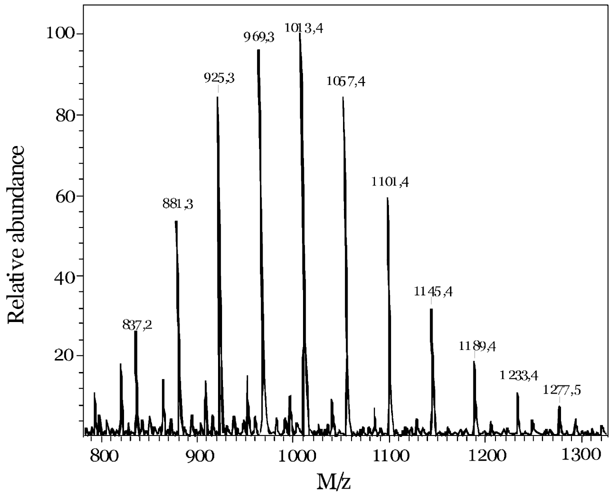

Fig. 12. ESI spectrum for oligourethane II-200b. (Table 3).

The results calculated theoretically and the findings from the GPC method are compared in Table 2. Good correlation can, in most cases, be observed for those two sets of data. The differences result from the fact that not only the principal oligomer—at the highest volume—is recorded in GPC chromatograms and MS spectra. Other high-molecular-weight products have also been observed and their volumes are much higher than those obtained from the balance. Moreover, chromatograms prove the presence of some amounts of unconverted monomers and oligomers with lower molecular weights, what could not be taken into consideration for theoretical calculations. Hence, the findings from the GPC analyses can be slightly overstated in relation to actual values.

5. Conclusions

As comes from the literature reports, developing new methods of synthesis for isocyanate and hydroxyl intermediates can be found useful for the manufacturing processes capable of yielding, for example, new types of elastomers, coatings and aqueous emulsions of PUs. The two-stage bulk polyaddition process of diisocyanates and polyols, which is most frequently employed, will not produce any well-defined and regular segmented structure. This is most probably not only because of chain irregularities (imperfection) but also due to considerable polydispersity of chemical composition and MWD of thus obtained linear PUs. That is typical for the equilibrium polymerisation process in which many molecules are present at every moment in the reaction system—basically monomers at the beginning, and then oligourethanes which are progressively produced and which simultaneously decay over time. The need to extend the prepolymer chains afterwards with the use of low-molecular-weight compounds makes the composition of the polyurethane mixture even more complicated. It is, hence, justified to develop a method which can give us all a tool to much better control the structure and that means to control the properties of polyurethanes.

The computer simulation based on the kinetic model for the step-by-step polyaddition process was found useful in developing grounds for the polyaddition process capable of yielding linear urethane oligomers with –OH and –NCO terminal groups and narrow MWDs. Our studies proved that those products could be obtained in a multi-staged polyaddition process of 2,4-TDI and 2,6-TDI with various hydroxyl compounds: low-molecular-weight diol (BD), polyethers (POG) or polyesters (PCD), with the excessive amount of one reacting substance employed. These reactions can be carried out in bulk, with no external catalyst, in

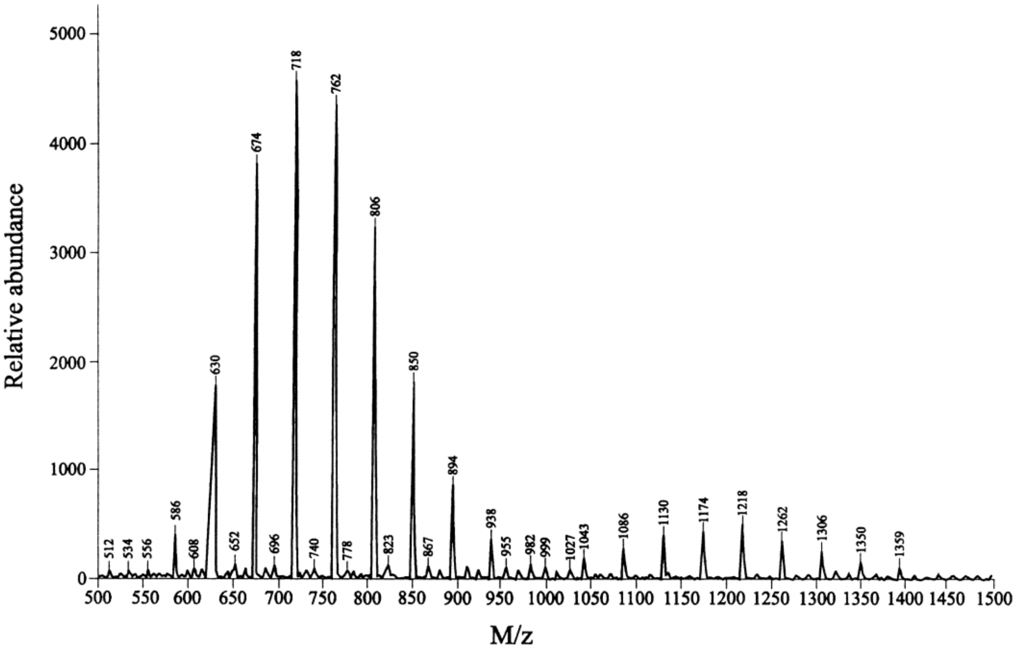

Fig. 13. MALDI-TOF spectrum for oligourethane I-300b (Table 3).

the presence of benzoyl chloride which stabilises urethane–isocyanate prepolymers produced. However, it is necessary to separate excess amounts of monomers after every process stage—that can be done by means of selective extraction methods.

The structural studies involved the GPC as well as IR, ESI and MALDI-TOF spectrometry methods and they could identify all intermediates—urethane oligomers which were progressively produced and which simultaneously decayed in the step-by-step polymerisation process. Chemical structures of oligourethanes obtained from the same polyols at odd stages (isocyanate prepolymers) and at even stages (urethane–hydroxyl prepolymers) were—as expected—much similar within particular groups of compounds, and the essential differences refer to the molecular sizes of oligomers. The presence of unconverted monomers clearly affects the viscosity specifications of the products obtained from downstream stages of the polymerisation process. After thorough purification of products, said viscosity is dependent on molecular weight of polyol employed in the reaction and on the process stage which yielded the product in question.

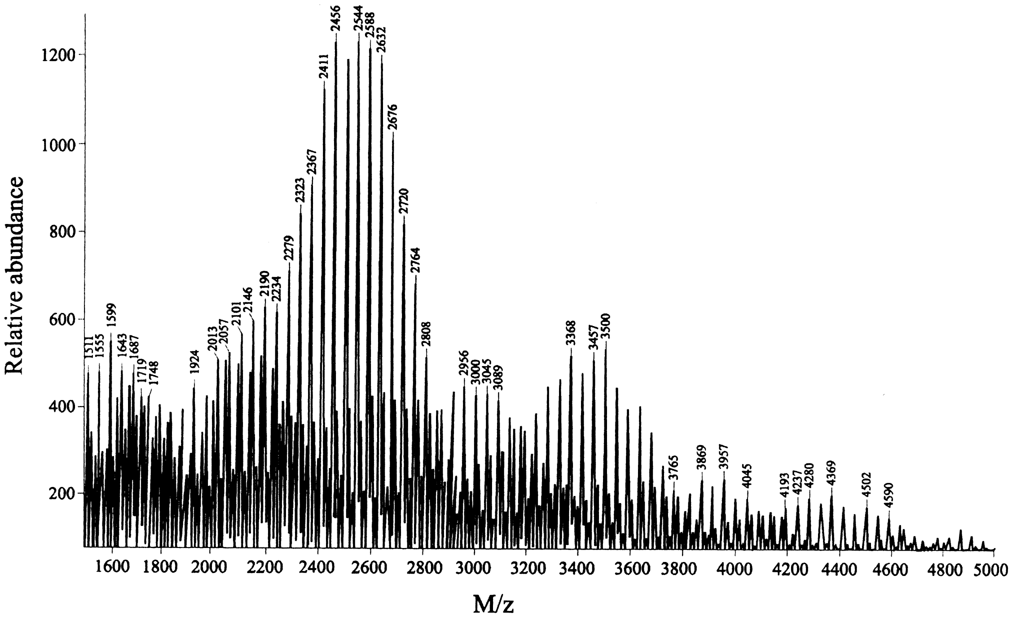

Fig. 14. MALDI-TOF spectrum for oligourethane V-300b (Table 3).

One dominant oligourethane is usually observed in the polymer mixture obtained after the first two polyaddition stages. Its structure is determined by the adopted stoichiometry. Chemical compositions of products from further stages become much more complex. Hence, the stoichiometric ratio is rather decisive for the type of terminal functional groups than for the reaction selectivity. The expected oligomer is always accompanied by a few other products which can be present even at comparable concentrations. It happens frequently that some small amounts of high-molecular-weight products appear as early as at the initial two stages of the process. These compound, however, always have identical end groups: −NCO or −OH.

It is possible to restrain the polydispersity degrees for the obtained oligomers to the range of 1.1–1.3, and—what is significant—no clear increase in MWD is observed with the progress of the polyaddition stage.

The findings for −NCO group contents and quantitative determinations with the GPC method confirmed the general consistence of expected chemical compositions of oligomers and the data calculated on the basis of mass balances for individual process stages.

Since excessive amounts of one of monomers need to be separated after every process stage, this method is applicable for semi-commercial plants of big laboratory stands to produce oligourethanes with precisely defined

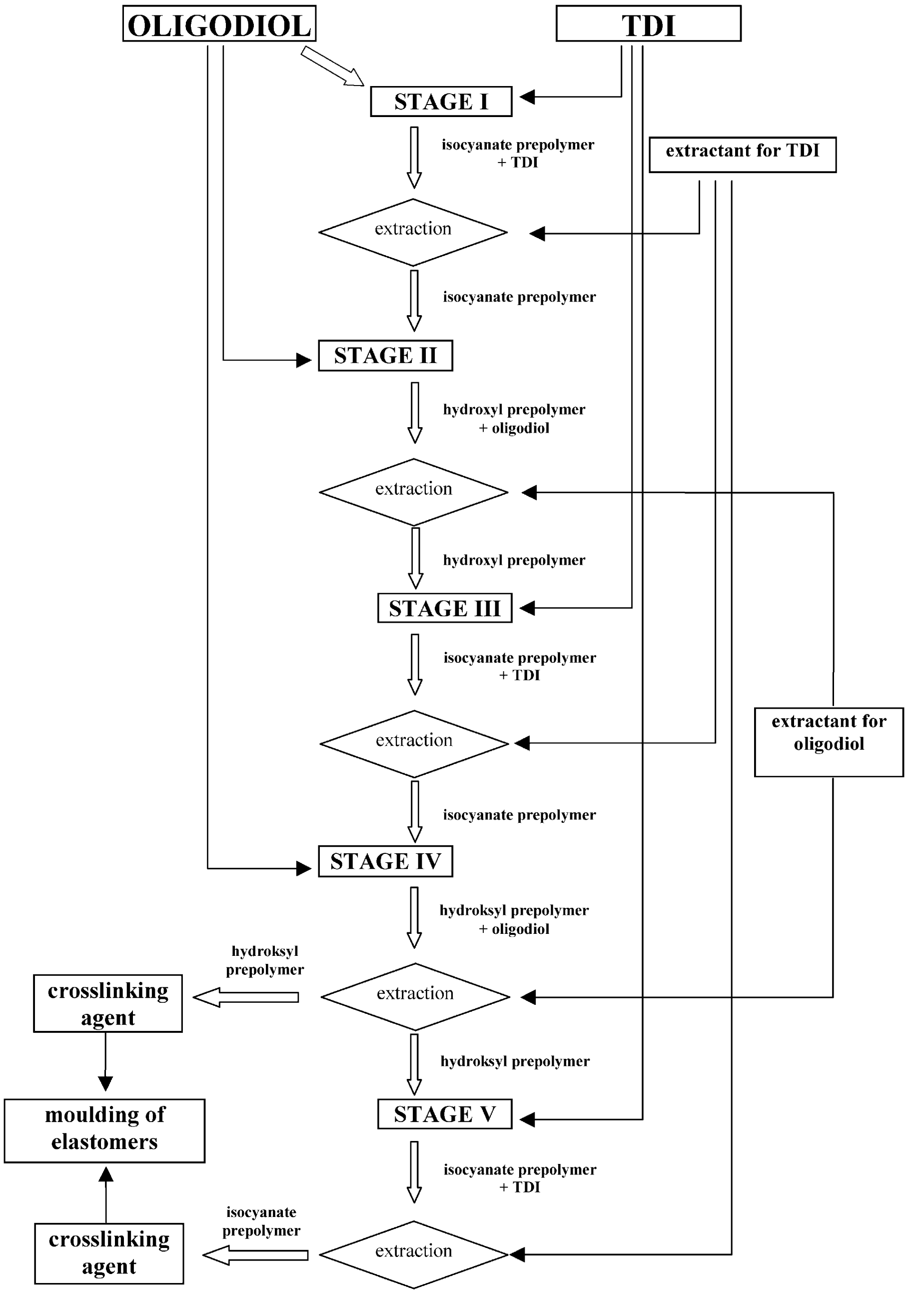

Fig. 15. Flow diagram for the process which yields polyurethanes with controlled molecular weights.

chemical compositions and regular chain structures. Such products can then be further processed, i.e. expanded to form linear polyurethanes with narrow MWDs and subjected to cross-linking, to yield foamed plastics or elastomers, e.g. with the RIM technique, or they can be used as macro-urethane cores on which chains of vinyl polymers can be grafted. The future process arrangement(s) must recycle separated monomers to the loop. The idea of such a process was presented in a diagram (Fig. 15) [29].

Then, it will be necessary to reveal the effect(s) of chemical structures of PUs synthesised from oligourethanes presented herein on supermolecular structures and thermal–mechanical properties of those PUs against PUs synthesised from the same feedstocks but in a single-stage method.

Acknowledgements

The authors which to thank Prof. Jerzy Silbering from the Jagiellonian University in Cracow, Faculty of Chemistry, for taking ESI spectra of the oligomers produced, and Mr Witold Pękala M.Sc., who translated this study into English.

This study was performed within the research project No. 3T09B 100 20 which was financially supported by the Committee for Scientific Research in Warsaw.

References

[1] Bernacca GM, Gulbransen MJ, Wilkinson R, Wheatley DJ. Biomaterials 1998;19:1151.
[2] US Patent No. 5786426; 1998.
[3] Pohl M-M, Dany R, Mix R, Gähde J, Hinrichsen G. Polymer 1996;37:2173.
[4] Zhang B, Tan H. Eur Polym J 1998;34:571.
[5] Park YS, Kang YS, Chung DJ. e-Polymers 2002, no. 016. http://www.e-polymers.org.
[6] Anzlovar A, Anzur I, Malavasic T. Polym Bull 1997;39:339.
[7] US Patent No. 5747392; 1998.
[8] Kim BK, Tharanikkkasu K, Lee JS. Colloid Polym Sci 1999;277:285.
[9] Jagur-Grodzinski J. React Funct Polym 2001;49:1.
[10] Flory P. Principles of polymer chemistry. Cornell V. Press; 1952.
[11] Król P, Pilch-Pitera B. Eur Polym J 2001;37:251.
[12] Król P, Pilch-Pitera B. Eur Polym J 2003;39:1229.
[13] Li F, Zuo J, Dong L, Weng H. Eur Polym J 1998;34:56.
[14] Yilgör E, Yurtsever E, Yilgör I. Polymer 2002;43:6551.
[15] Król P. Int Polym Sci Technol 1997;24:100.
[16] Król P, Heneczkowski M. Polimery 2000;45:775.
[17] Król P, Galina H, Kaczmarski K. Macromol Theory Simul 1999;8:129.
[18] Król P, Pilch-Pitera B. Polimery 2002;47:77.
[19] Stagg FE. Analyst 1966;71:557.
[20] US Patent No. 3883577; 1975.
[21] Furer VL. J Mol Struct 2000;520:117.
[22] Zha L, Wu M, Jang J. J Appl Polym Sci 1999;73:2895.
[23] Semsaderzadeh MA, Navarchian AH. J Polym Engng (2002), report presented for publication.
[24] Hatas J, Krawiecki C. Polimery 1979;34:440.
[25] Yontz DJ, Hsu SL. Macromolecules 2000;33:8415–20.
[26] Rokicki G, Piotrowska A. Polymer 2002;43:2927–35.
[27] Esser E, Keil C, Braun D. Polymer 2000;41:4039–404.
[28] Prochazka F, Nicolai T, Durand D. Macromolecules 2000;33:1703–9.
[29] Pilch-Pitera B. Synthesis of urethane oligomers as intermediates for the production of polyurethanes with controlled molecular weight distribution. Doctor's Thesis, Rzeszów University of Technology; 2003.