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A study on the synthesis of urethane oligomers

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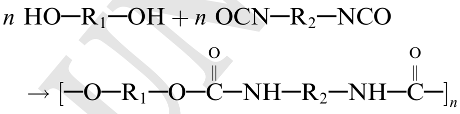
Abstract

A method of preparation of isocyanate- or hydroxy-terminated urethane oligomers of narrow molecular weight distribution was developed and the products used for preparation of polyurethane elastomers. The method consists of the controlled step-wise reaction of 2,4- and 2,6-toluene diisocyanate (TDI) with butan-1,4-diol (BD) (in the first step) or with polyoxyethylene glycols of molecular weight varying from 200 to 1000 (following steps). All reactions were carried out in bulk. The clue was that the isocyanate- or hydroxy-terminated oligourethanes obtained in a previous step were used as the substrates in the next preparation step where they reacted with an excess of appropriate glycol or TDI, respectively. The unreacted monomer excess was removed by extraction. The products of subsequent steps characterized by spectral analysis IR and NMR and their molecular weight were determined by matrix-assisted laser desorption ionization–time of flight and electrospray ionization mass spectroscopy and gel-permeation chromatography. The oligomers were cross-linked with trifunctional low-molecular chain extenders yielding polyurethane elastomers.

1. Introduction

In one of our earlier works [1], we presented a new approach to the step-wise polyaddition of diisocyanates and polyols that yielded linear polyurethanes of controlled composition and molecular weight. The method consisted of programmed synthesis derived from the kinetic scheme of subsequent-parallel reactions. The scheme had a specific form suitable for the classical polyaddition equation:



$$n\,\mathrm{HO{-}R_1{-}OH} + n\,\mathrm{OCN{-}R_2{-}NCO} \rightarrow [\mathrm{{-}O{-}R_1{-}O{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}NH{-}R_2{-}NH{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}}]_n \quad (1)$$

where R_1 is an aliphatic or aromatic moiety constituting a polyether or polyester part of a diol, R_2 is an aliphatic, cycloaliphatic, or aromatic fragment of diisocyanate.

By using an algorithm developed earlier [2,3], we have proposed a procedure of carrying out polymerization of 2,4- and 2,6-toluenediisocyanate (TDI) and butan-1,4-diol (BD) in which creates a polyurethane mixture consisting of isocyanate- or hydroxy-terminated oligourethanes. Depending on the particular stage of synthesis, the oligomeric substrate was treated with an excess of a glycol or diisocyanate. The linear polymer obtained after several stages of addition was expected to have predictable chemical structure and limited polydispersity. The limited polydispersity was achieved by carefully removing the excess of reagents, i.e., TDI or BD that have not reacted, right after each step [4].

The polyaddition steps were carried out in the presence of THF to prevent any uncontrolled processes due to excessive viscosity of the system. The problem of viscosity control was of primary importance in Ref. [1]. The composition of mixtures obtained at each reaction stage was verified by comparing GPC data with values calculated numerically. We intended to apply the same procedure for the more feasible synthesis of polyurethanes in bulk.

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Thus, we prepared linear polyurethanes terminated with hydroxyl or isocyanate groups that could then be extended with low-molecular compounds: diols or diamines or could be cross-linked with triisocyanates [1].

The novel oligourethane hydroxyl or isocyanate terminated semiproducts seem to be a desirable component of polyurethane elastomers or aqueous emulsions [5]. Furthermore, urethane-hydroxyl oligomers have markedly improved shelf-storage stability and are less toxic than not only the diisocyanate monomers, but also isocyanate oligomers [6].

Polyrethane elastomers are usually prepared from expensive raw materials: 1,4-*trans*-cyclohexane diisocyanate, 1,5-napthylene diisocyanate, or mixtures of 4,4′-diphenylmethane diisocyanate with its hydrogenated analogue 4,4′-dicyclohexylmethane diisocyanate. The polyol components are, e.g., a polytetramethylene glycol (polytetrahydrofuran) or polyester of regular chain structure [7–14]. The reason is that the cheapest and most popular system comprising TDI and oligoxyalkylenedioles does not produce the appropriate segmental structure, not only because of irregularities of chains, but also because of high polydispersity of the linear fragments of polyurethane.

This polydispersity is typical of the Flory-type polycondensation systems. Further extension of chains by low-molecular compounds adds up to the complexity of the system.

The step-wise successive method of synthesis of hydroxyl or isocyanate terminated prepolymers was used in this work for preparation of polyurethane oligomers from higher polyoxyethylene glycols (POG). The reaction was carried out in bulk, without any solvent. Of particular importance was to develop an effective method of removal of unreacted monomers in each step of oligomer growth. A selective extraction method was used to achieve this goal. This made it possible to control the molecular weight distribution (MWD) of the resulting products.

1.1. Synthesis of urethane oligomers

The step-wise method of preparing urethane oligomers from BD or POG of molecular weight 200, 400, 600, and 1000 g/mol and from 2,4- and 2,6-TDI differed significantly from that previously described [1] by the lack solvent. Hence, a modification of the procedure consisted in carrying out the reactions in bulk. The mixture of products at each step is to be freed from the excess of monomer. As in the previous system [1], the process is described by the sequence of subsequent-parallel irreversible reactions:

$$
\begin{aligned}
&\mathrm{A} + x\mathrm{B} \rightarrow \mathrm{A}_1\mathrm{B}_2 + (x-2)\mathrm{B}\\
&\mathrm{A}_1\mathrm{B}_2 + x\mathrm{A} \rightarrow \mathrm{A}_3\mathrm{B}_2 + (x-2)\mathrm{A}\\
&\mathrm{A}_3\mathrm{B}_2 + x\mathrm{B} \rightarrow \mathrm{A}_3\mathrm{B}_4 + (x-2)\mathrm{B}(2) \qquad (2)\\
&\text{etc.}\\
&\text{for } x \gg 1
\end{aligned}
$$

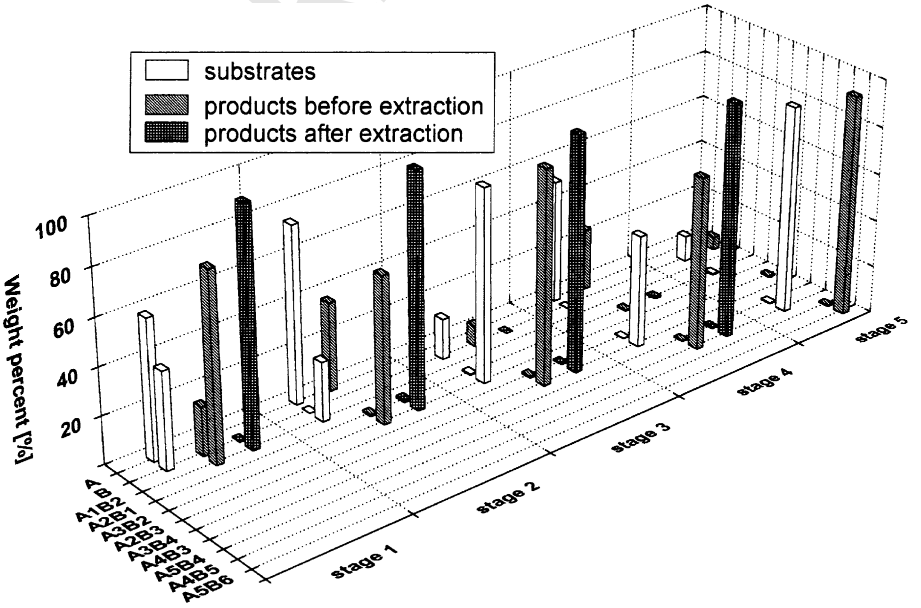

Fig. 1. Weight percentages for the reaction products as referred to the total amounts of PU and monomers at the successive stages of the process involving TDI and polyethylene glycol ($M_n = 1000$ g/mol).

In Scheme (2) A stands for BD or POG, B denotes the isocyanate monomer (2,4- lub 2,6- TDI), and A_nB_m is the oligourethane. The latter might a urethane-diol $A_{n+1}B_n$ or urethane-diisocyanate A_nB_{n+1}.

The addition process is always started with reaction with high excess of diisocyanate. To maximize the conversion and to make sure that at least 2 moles of the monomer introduced remained unreacted, each reaction of scheme (2) was carried out with 2-fold molar excess of the respective reagent—BD, POG, or TDI. The substrates were introduced under 'mild' conditions so chosen that possibly no side reactions of isocyanate groups took place, such as formation of allophanate links or cyclization to isocyanurates. No catalyst was used, either. After each stage, the excess of unreacted monomers was removed by extraction. The purified product A_nB_m was then used in the next polymer construction step. The monomer extracted was recovered after the solvent was distilled off. The main objective of the procedure was to limit the distribution of molecular weights of the linear polyurethane molecules. Benzoyl chloride acting as the acidity stabilizer was used to extend the stability of prepolymers A_nB_{n+1} before they were used on the next step of the procedure.

The calculated compositions of substrates and of reaction products are presented in Fig. 1. The calculations were based on the stoichiometry of each reaction and on the analytically measured amount of reactive —NCO groups in isocyanate prepolymers or on the mass reduction of the samples after extraction. A comparison of the contents of free —NCO was additionally presented in Fig. 2, and that of glycols in Table 1.

Table 1
Comparison contents of free glycols

No. of sample as per Table 2	Content of free glycol (%)
2bBD	Glycol was removed completely
2b200	50.98
4b200	70.55
2b400	16.13
4b400	17.38
2b600	Glycol was removed completely
2b1000	Glycol was removed completely
4b1000	Glycol was removed completely

2. Experimental

2.1. Raw materials and reagents

- 2,4 i 2,6 TDI (toluene diisocyanate). A commercial product was used in the study. It was a mixture of 2,4- and 2,6- TDI isomers at the ratio of 80% and 20%, respectively, from Aldrich.
- Polyoxyethylene glycol $M_n = 200, 400, 600$ and 1000 g/mol from Aldrich. The glycols was dried under vacuum in nitrogen atmosphere, in temperature 110 °C during 2 h.
- Triethanoloamine (pure) from POCh-Gliwice, Poland.
- 1,1′,1″-Methylidynetris[4-isocyanatobenzene] (DESMODUR RF) (commercial product) in 1,2-dichloroethane from Bayer A.G., Germany.
- Benzoyl chloride (pure) from POCh-Gliwice, Poland.
- 1,4-Butanediol (pure) from Aldrich.
- The solvents: hexane, ethyl acetate, toluene, xylene, carbon tetrachloride, and tetrahydrofuran were reagent grade and supplied by POCh-Gliwice, Poland.

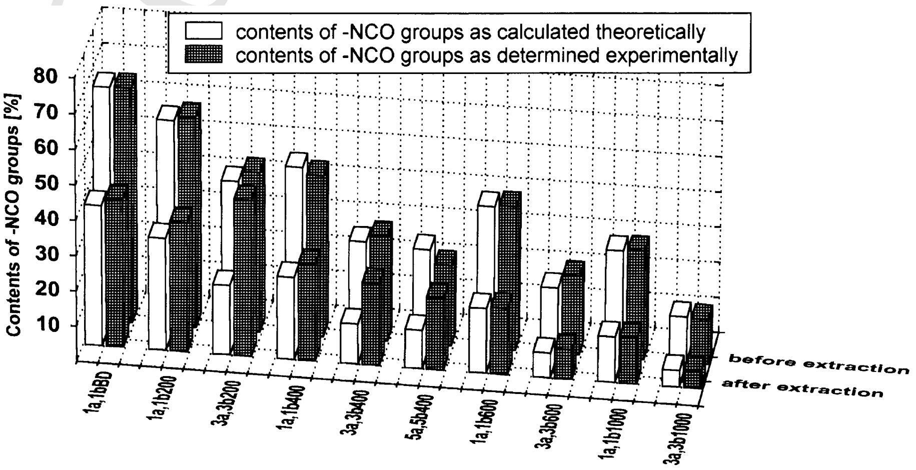

Fig. 2. Comparison for the contents of free —NCO groups versus calculated values before and after extraction.

2.2. Method of the synthesis of urethane oligomers

The reactions were carried out in bulk in a glass reactor under nitrogen with benzoyl chloride (0.3 wt.% with respect to TDI) that stabilized viscosity of the reagent. A calculated amount of hydroxyl- or isoacyanate-terminated oligomer prepared in earlier stage was introduced drop-wise to TDI or appropriate glycol, respectively. It was always the minority component that was introduced to excess reagent. The time of introduction was adjusted to last approximately 30 min. The reacting mixture was kept at 65 ± 1 °C. This temperature was kept for another 2 h after completing introduction of the minority component. Then, viscosity of the product was measured and, when appropriate, also the amount of isocyanate groups. The changes in viscosity are presented in Fig. 3.

A comprehensive scheme of the synthesis of linear polyurethanes is presented in Table 2. Letter 'a' denotes the samples taken straight from the reactor, while letter 'b' denotes the products after extracting out the excess of TDI or diol. If the products could not for some reasons be isolated, the products were marked with minus sign. Otherwise, the samples have the plus.

The excess of majority reagent was extracted out after each reaction stage. The solvents were individually selected for each stage since the solubility of the products have changed. The choice of the appropriate solvent was a subject of a separate experiment. The results were obtained by using hexane–ethyl acetate 2:1 or 1:1 mixtures in the case of TDI extraction. The amount of ethyl acetate was increased as increased the molecular weight of POG used.

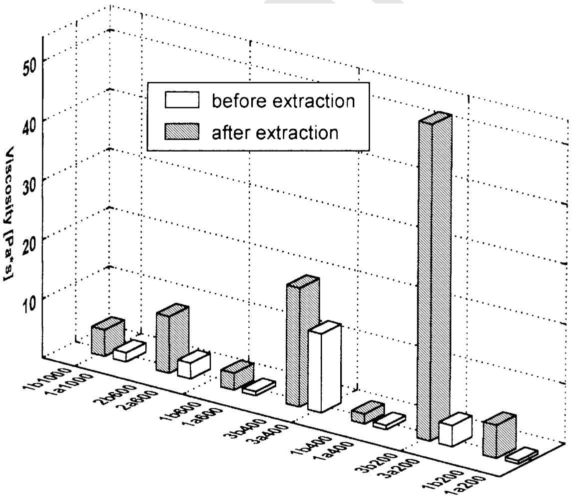

Fig. 3. Comparison of viscosity figures for prepolymers before and after extraction.

The excess of BD was removed with water and that of POG 400 or 600 with toluene. POG 60 was tretaed with a mixture of xylene and toluene, and POG 1000 with CCl_4 (Table 2).

The 'final' oligomer samples were cross-linked with trifunctional compounds: triethanoloamine or Desmodur RF. The testing specimens were cast in closed teflon molds with silicone separator after degasing the prepolymer mixture. The specimens were subjected to further investigation. DSC curves for the cross-linked PU obtained were presented in Figs. 11 and 12.

2.3. Analytical methods

2.3.1. NCO group contents

The typical dibutyl amine method was used. The excess of unreacted dibutylamine was titrated with aqueous HCl against bromophenyl blue. The results are compared with calculated data in Fig. 2.

2.3.2. Viscosity measurements

The dynamic viscosity of oligomers A_nB_m was determined at 25 °C by using a rotational Rheotest 2 viscometer (Rheotest GmbH). Cylinders of H type were were used at the revolution range 3b to 12a (range I), depending on the type of product. Practically no dependence of viscosity on shear rate was observed. The results are presented in Fig. 3.

2.3.3. Mass spectrometry

The mass spectra of the resulting polyurethane oligomers were recorded on an electrospray ionization spectrometer (ESI MS) Finnigan MAT 95S (Germany) and on a matrix-assisted laser desorption ionization–mass spectrometry (MALDI MS) spectrometer. ESI spectra were obtained by using KJ solution for ionization. The mobile phase ($CH_3OH + THF$) flow rate was 5 μdm³/min. Only the positive ions were recorded in the range 200–2000 M/z enlarged by the mass of K^+(39) or Na^+ (23) originating essentially from impurities. The samples were diluted with methanol to the concentration of pikomoles/dm³.

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/cm³). The samples were also dissolved in THF (to conc. 1 mg/cm³) and NaJ in acetone (10 mg/cm³) was added. Ions of mass increased by molecular weight of Na or K were recorded. The results of mass spectrum analysis are listed in Table 3.

Table 2
Specification for polyaddition processes studied

Sample number	No. of stage	Sample availability	Type of extrahents	Principal reaction in this process	M_A
1aBD	1	+			90
1a200		+			200
1a400		+		$A + 4B \rightarrow A_1B_2 + 2B$	400
1a600		+			600
1a1000		+			1000
1bBD		+			90
1b200		+	Hexane + ethyl acetate 2:1	$A_1B_2 + 2B \xrightarrow[-2B]{Ex_1} A_1B_2$	200
1b400		+			400
1b600		+			600
1b1000		+	Hexane + ethyl acetate 1:1		1000
2aBD	2	+			90
2a200		+		$A_1B_2 + 4A \rightarrow A_3B_2 + 2A$	200
2a400		+			400
2a600		+			600
2a1000		+			1000
2bBD		+	Water		90
2b200		+	Toluene	$A_3B_2 + 2A \xrightarrow[-2A]{Ex_2} A_3B_2$	200
2b400		+	Toluene		400
2b600		+	Xylene + toluene 1:1		600
2b1000		+	Carbon tetrachloride		1000
3aBD	3	+			90
3a200		+		$A_3B_2 + 4B \rightarrow A_3B_4 + 2B$	200
3a400		+			400
3a600		+			600
3a1000		+			1000
3bBD		–	Hexane + ethyl acetate 2:1	$A_3B_4 + 2B \xrightarrow[-2B]{Ex_3} A_3B_4$	90
3b200		+			200
3b400		+			400
3b600		–			600
3b1000		+	Hexane + ethyl acetate 1:1		1000
4aBD	4	–			90
4a200		+		$A_3B_4 + 4A \rightarrow A_5B_4 + 2A$	200
4a400		+			400
4a600		–			600
4a1000		+			1000
4bBD		–	–		90
4b200		+	Toluene	$A_5B_4 + 2A \xrightarrow[-2A]{Ex_4} A_5B_4$	200
4b400		+	Toluene		400
4b600		–	–		600
4b1000		+	Carbon tetrachloride		1000
5aBD	5	–			90
5a200		+		$A_5B_4 + 4B \rightarrow A_5B_6 + 2B$	200
5a400		+			400
5a600		–			600
5a1000		+			1000
5bBD		–	Hexane + ethyl acetate 1:1	$A_5B_6 + 2B \xrightarrow[-2B]{Ex_5} A_5B_6$	90
5b200		–			200
5b400		+			400
5b600		–			600
5b1000		–			1000

Table 3
Interpretation of mass spectra for PU oligomers

Number of sample as per Table 1	Type of MS method	Location of band (M/z)	Relative intensity of band (%)	Probable structure of molecular ion	Calculated molecular weight (g/mol)
1bBD	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
2bBD	MALDI	378	22.22	$A_2\ B_1\ +Na^+$	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
3bBD	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	7.7	$A_5B_6 + Na^+ + 2CH_3OH$	1582.02
		1848	1.92	$A_6B_7 + Na^+ + 2CH_3OH$	1846.19
Polyethylene glycol $M_n = 200$ g/mol	ESI	409.1	100	$A + K^+$	409 ($n = 8$)
		365.1	88	$A + K^+$	365 ($n = 7$)
1b200	ESI	689.2	100	$A_1B_2 + Na^+$	692.34 ($n_1 = 6$)
2b200	ESI	365.1	100	$A + K^+$	365 ($n = 7$)
		969.3	97	$A_3B_2 + K^+$	969.34 ($n_{1-3} = 4$)
		1013.4	100	$A_3B_2 + K^+$	1013.34 ($n_{1,2} = 4$, $n_3 = 5$)
3b200	ESI	689,2	100	$A_1B_2 + Na^+$	692.34 ($n_1 = 6$)
4b200	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 ($n_{1-3} = 4$)
5b200	ESI	689,2	94	$A_1B_2 + Na^+$	692.34 ($n_1 = 6$)
		733,2	100	$A_1B_2 + Na^+$	736.34 ($n_1 = 7$)
Polyethylene glycol $M_n = 400$ g/mol	ESI	497.2	100	$A + K^+$	497 ($n = 10$)
1b400	ESI	849.3	100	A_1B_2	850 ($n_1 = 11$)
2b400	ESI	497.2	100	$A + K^+$	497 ($n = 10$)
3b400	ESI	849.1	100	A_1B_2	850 ($n_1 = 11$)
4b400	ESI	497,2	100	$A + K^+$	497 ($n = 10$)
5b400	ESI	583.2	100	$A_1B_1 + K^+$	583.17 ($n_1 = 8$)
		627.1	73	$A_1B_1 + K^+$	627.17 ($n_1 = 9$)
Polyethylene glycol $M_n = 600$ g/mol	MALDI	614	100	$A + Na^+$	613 ($n = 13$)
1b600	MALDI	875	100	$A_1B_2 + Na^+$	873.34 ($n_1 = 11$)
2b600	MALDI	570	100	$A + Na^+$	569 ($n = 12$)
		1335	7.8	$A_2B_1 + Na^+$	1337.17 ($n_1 = 12$, $n_2 = 13$)
		2143	46.1	$A_3B_2 + Na^+$	2141.34 ($n_{1-3} = 13$)
		2820	6.4	$A_4B_3 + Na^+$	2817.51 ($n_{1,2} = 12$, $n_{3,4} = 13$)
		3628	6.3	$A_5B_4 + Na^+$	3625.68 ($n_1 = 12$, $n_{2-5} = 13$)
Polyethylene glycol $M_n = 1000$ g/mol	MALDI	923	100	$A + Na^+$	921 ($n = 20$)
1b1000	MALDI	1272	100	$A_1B_2 + Na^+$	1269.34 ($n_1 = 20$)
2b1000	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 ($n_{1-3} = 20$, $n_4 = 21$)
3b1000	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*)

Number of sample as per Table 1	Type of MS method	Location of band (M/z)	Relative intensity of band (%)	Probable structure of molecular ion	Calculated molecular weight (g/mol)
		5098	2.94	$A_4B_5 + Na^+$	5101.85 ($n_{1,2} = 23$, $n_{3,4} = 24$)
4b1000	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	10.4	$A_4B_3 + H^+$	4643.51 ($n_{1–4} = 23$)
		5319	10.11	$A_5B_4 + H^+$	5319.68 ($n_{1,2} = 20$, $n_{3,4} = 21$)
5b1000	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 ($n_{1–5} = 20$, $n_6 = 21$)

2.3.4. Size exclusion chromatography

The MWD of the oligomer samples was determined by a KNAUER (Germany) gel chromatograph equipped with a system of 4 columns of the size 250 mm × 7.5 mm × 3 μm packed with PL-GEL MIXED E of pore diameters: 100, 1000, 10,000, and 100,000 Å. Refactive index (RI) detector was used. The measurements were carried out at 25 ± 0.1 °C and flow rate of eluate (THF) 0.8 cm^3/min. The chromatograms were interpretted basing on a special calibration method based on carbamates presented in Ref. [1]. The results are presented in Table 4.

Another size exclusion chromatography (SEC) 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 o the size 7.8 mm × 300 mm packed with TSK-gel of pore diameter 5 μm. The eluent (THF) flow rate was 1 cm^3/min, volume of inflow circuit was 20 μdm^3. The results were interpretted basing on the calibration [14] with polystyrene standard of $M_w = 5970$ g/mol and TriSEC GPC Software GPC–LS–Viscosimetry Module, Version 3.0 (1995–1998) by Viscotec Corporation.

2.3.5. Structural analysis

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

2.3.6. Thermal analysis

The thermal analysis was carried out on a STA-625 differential scanning calorimeter (Polymer Laboratories, England). The measurements were made in the range of −80 to +120 °C and nitrogen flow 30 cm^3/min. The heating rate was 20 °/min, and the cooling rate 11 °/min to temperature −60 °C and 1 °/min down to −120 °C.

3. Results and discussion

The results presented in Fig. 1 show the gradual increase of molecular weight of oligourethanes formed in the subsequent stage of polyaddition. This is also confirmed by the decrease of isocyanate groups in —NCO terminated samples (Fig. 2) as well as by the viscosity increase of the samples (Fig. 3).

The extraction procedure applied to remove the excess of monomers seemed to be efficient for most of the cases. One major component is present in each sample in consistency with the stoichiometry. From Fig. 2 it follows that the concentration of —NCO groups in isocyanate terminated oligomers both before and after extraction is close to the values calculated from stoichiometry. This also consistent with the substantial viscosity increase after the unreacted isocyanate monomer has been extracted out (Fig. 3).

The amount of diols was possible to estimate gravimetrically by comparing weights of samples before and after extraction. Due to the presence of —NH— groups

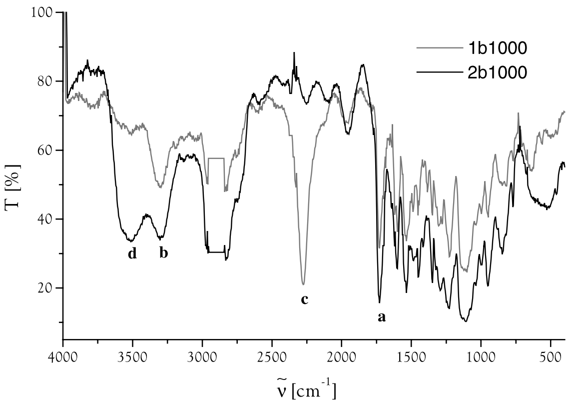

Fig. 4. IR spectrum for sample 1b1000 and 2b1000.

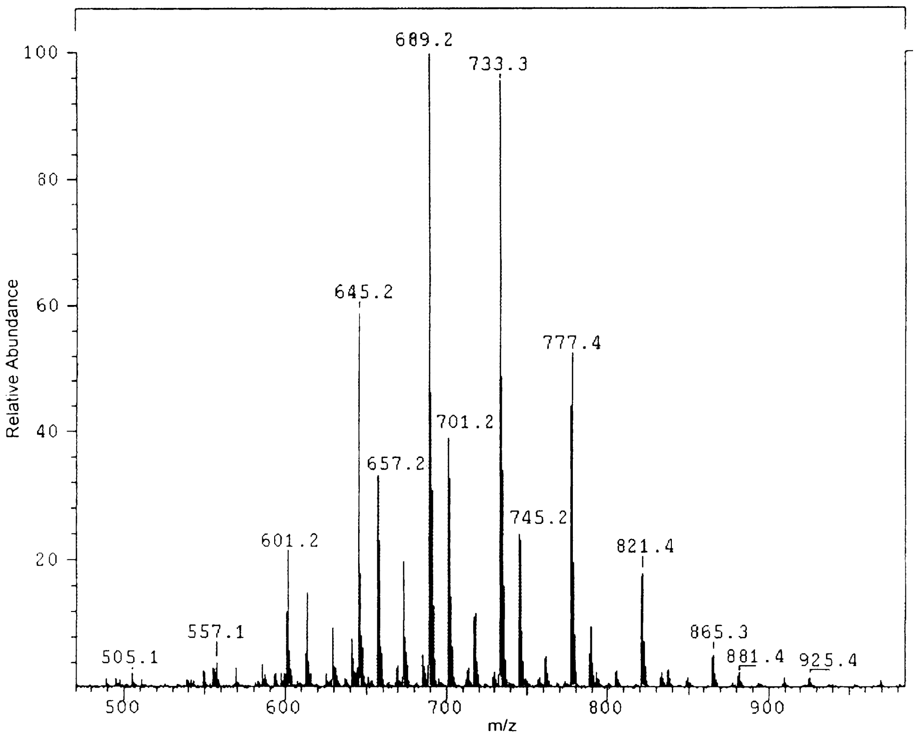

Fig. 5. MS (ESI) spectrum for prepolymer 1b200.

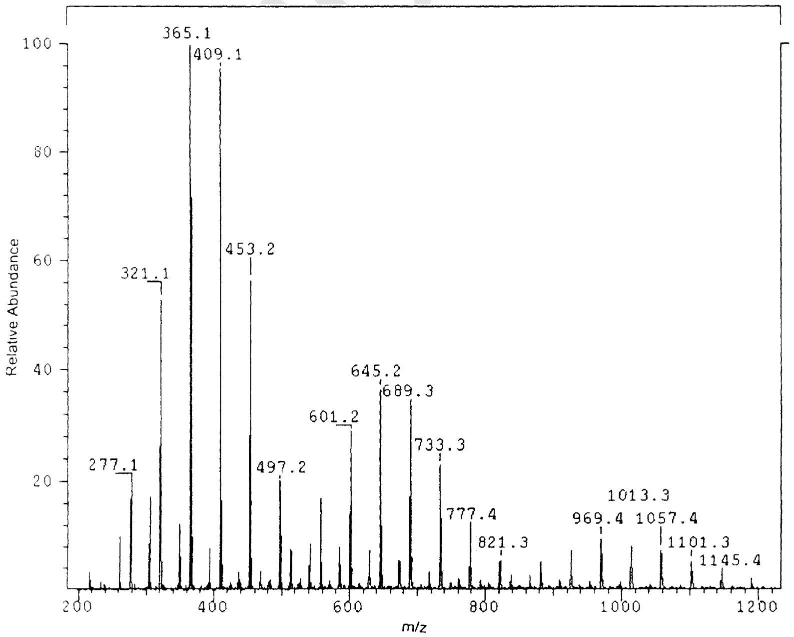

Fig. 6. MS (ESI) spectrum for prepolymer 3b200.

in oligomers, any direct and selective chemical determination of —OH by, say, acylation or phtalilation, was impossible. The results of estimation presented in Table 1 indicate that BD or glycols of $M_n = 600$ and 1000 g/

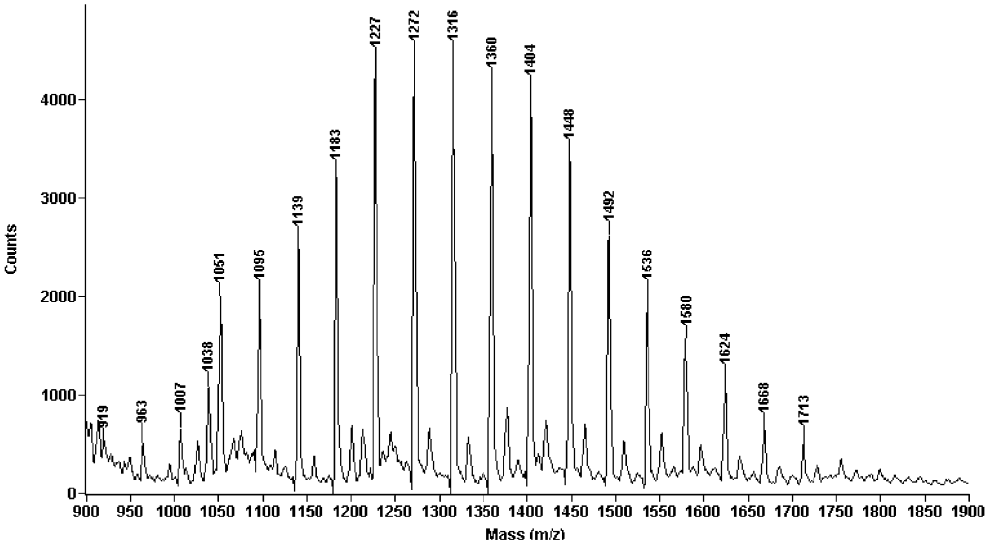

Fig. 7. MS (MALDI) spectrum for oligomer 1b1000.

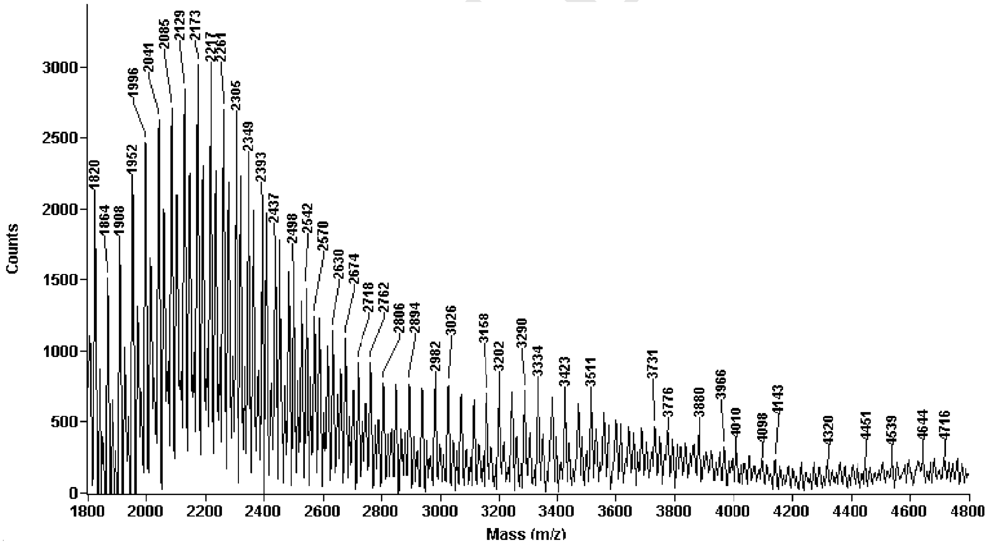

Fig. 8. MS (MALDI) spectrum for oligomer 3b1000.

mol were fully removed by extraction. POG 200 and 400 were unfortunately not fully removed. Probably the viscosity increase in the final stages of addition prevented full extraction.

The spectra in Fig. 4 fully confirm the anticipated structure of products. The characteristic bands at approximately 1730 (a) and 3300 cm^{-1} (b), due to stretching vibration of carbonyl and imine groups, respectively, confirm the presence of urethane grouping —NHCOO—. The extra band at approximately 2272 cm^{-1} (c) due to —NCO groups is present only in the isocyanate-terminated products A_nB_{n+1}, whereas the band at 3450 cm^{-1} (d) comes from hydroxy-terminated oligomers $A_{n+1}B_n$. All these bands appear in oligourethanes A_nB_n.

Further detailed information on the chemical composition of the samples was obtained from MS and SEC. The MWD of glycols and hydroxy-terminated prepolymers is presented in Table 3. The measured molecular masses are in good agreement with calculated ones. For

Table 4
Interpretation of GPC chromatograms for PU oligomers

No. of sample as per Table 1	Type of GPC chromatograph	M_n in peak maximum	M_n calculated (g/mol)	Type of oligomer	Percentage (weight) of oligomer (wt.%)
Butan-l,4-diol	Viscotec	91	90	A	100
2bBD	Viscotec	288	354	A_2B_1	1.59
		619	618	A_3B_2	48.02
		960	1056	A_5B_4	9.26
		1479	1410	A_6B_5	33.95
		2350	2286	A_8B_9	7.19
3aBD	Viscotec	115	174	B	2.73
		372	438	A_1B_2	3.12
		973	966	A_3B_4	56.19
		1622	1758	A_6B_7	37.96
Polyethylene glycol $M_n = 200$ g/mol	Knauer	126			1.26
		206	206	A	56.48
		258			42.26
1b200	Knauer	284	174	B	1.8
2b200	Knauer	458	554	A_1B_2	62.15
		823	934	A_2B_3	36.05
		247	206	A	2.74
		541	586	A_2B	3.77
		787	966	A_3B_2	50.82
		1269	1346	A_4B_3	42.68
3b200	Knauer	278	174	B	3.74
		451	554	A_1B_2	25.51
		1000	1296	A_3B_4	51.30
		1455	1671	A_4B_5	19.45
4b200	Knauer	126			0.62
		192	206	A	0.85
		261			3.32
		544	586	A_2B	9.53
		828	966	A_3B_2	24.77
		1335	1322	A_4B_3	38.31
		1744	1696	A_5B_4	22.60
5b200	Knauer	306	174	B	7.93
		484	554	A_1B_2	34.99
		800	934	A_2B_3	15.73
		1086	1296	A_3B_4	19.57
		1601	1671	A_4B_5	21.78
Polyethylene glycol $M_n = 400$ g/mol	Knauer	371	370	A	100
1b(400)	Knauer	307	174	B	2.38
		626	718	A_1B_2	56.60
		1062	1262	A_2B_3	31.39
		1451	1806	A_3B_4	9.63
2b400	Knauer	409	370	A	8.39
		1229	1458	A_3B_2	51.92
		1871	2002	A_4B_3	39.69
3b400	Knauer	309	174	B	1.14
		655	718	A_1B_2	18.53
		1075	1262	A_2B_3	9.28
		1479	1806	A_3B_4	30.89
		1919	2350	A_4B_5	37.92

Table 4 (*continued*)

No. of sample as per Table 1	Type of GPC chromatograph	M_n in peak maximum	M_n calculated (g/mol)	Type of oligomer	Percentage (weight) of oligomer (wt.%)
		2941	2894	A_5B_6	2.24
4b400	Knauer	398	370	A	4.16
		1229	1458	A_3B_2	22.87
		1944	2002	A_4B_3	40.87
		2550	2551	A_5B_4	32.10
5b400	Knauer	582	544	A_1B_1	12.10
		1340	1806	A_3B_4	21.00
		2013	2350	A_4B_5	37.57
		2450	2895	A_5B_6	29.33
Polyethylene glycol $M_n = 600$ g/mol	Viscotec	589	590	A	100
1b600	Viscotec	940	938	A_1B_2	70.78
		2642	2466	A_4B_3	29.22
2b600	Viscotec	1153	1354	A_2B_1	11.67
		2119	2118	A_3B_2	47.99
		2511	2882	A_1B_2	40.34
3a600	Viscotec	93	174	B	0.58
		813	938	A_1B_2	12.13
		1871	1702	A_2B_3	36.40
		2432	2466	A_3B_4	50.89
Polyethylene glycol $M_n = 1000$ g/mol	Viscotec	1000	986	A	100
1b1000	Viscotec	1328	1334	A_1B_2	30.58
		2285	2494	A_2B_3	69.42
2b1000	Viscotec	1330	986	A	3.39
		1698	2070	A_2B_1	10.64
		3306	3306	A_3B_2	85.98
3b1000	Viscotec	2107	2494	A_2B_3	0.69
		3704	3654	A_3B_4	18.20
		4794	4814	A_4B_5	81.11
5a1000	Viscotec	4677	4814	A_4B_5	4.60
		5370	5626	A_5B_4	20.47
		6026	5974	A_5B_6	74.92

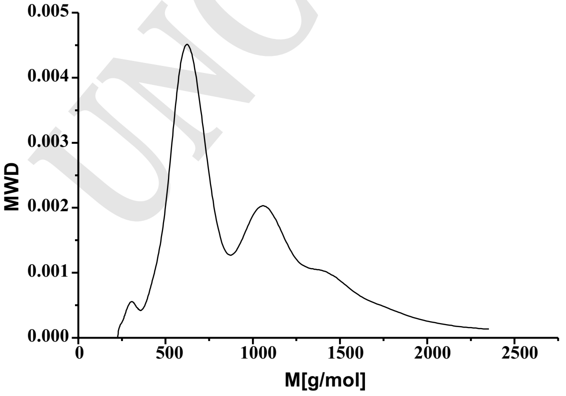

Fig. 9. Chromatogram for sample 1b400.

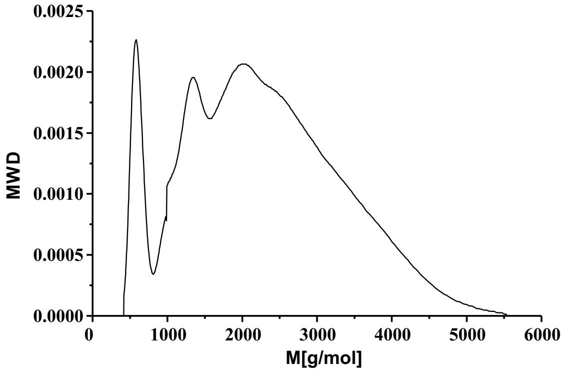

Fig. 10. Chromatogram for sample 5b400.

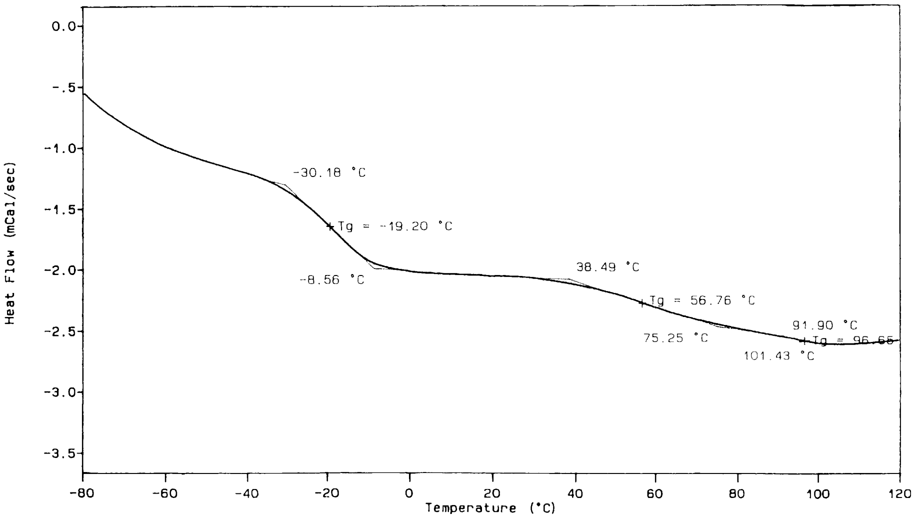

Fig. 11. DSC curve for PU obtained from the oligomer 1b1000 and triethanolamine.

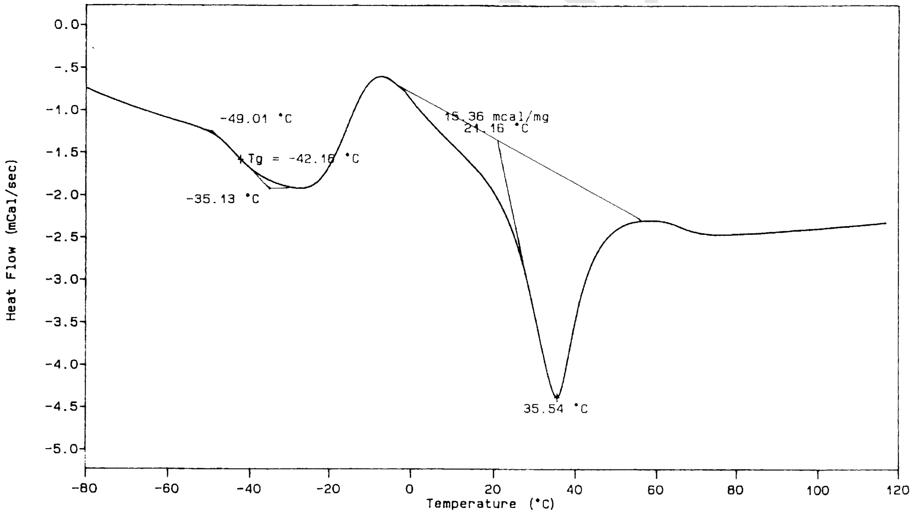

Fig. 12. DSC curve for PU obtained from the oligomer 2b1000 and Desmodur RF.

glycol POG 200, however, the value of M/z has been found higher than expected, namely 409. Each spectrum contains a series of peaks separated by the value of 44, in agreement with the mass of oxyethylenic group $-CH_2CH_2O-$. The position of the signal of the highest intensity is specified in Table 3. The spectra obtained by ESI technique (Figs. 5 and 6) show the distribution only in the range up to 1200 M/z, i.e., in the range insufficient for the present samples. Missing information became available from the SEC analysis. Matrix-assisted laser desorption ionization–time of flight technique (Figs. 7 and 8) yields fuller characteristics of the distribution than ESI.

Concluding one may state that the chemical composition of the polyurethane oligomers obtained by the step-wise method of synthesis is much more complicated than one might expect basing on theoretical assumptions. In the products of several series of addition operations not only monomeric components are present that extraction failed to remove completely, but also oligomers of low-molecular weight.

Basing on the chromatograms (Table 4) one can conclude that in the initial stages of addition the main products are the expected ones. Some amount of bigger molecules is also formed (Fig. 9). For example, beside prepolymer A_1B_2, also oligomers A_2B_3 and A_3B_4 are present. In the later stages (Fig. 10), beside the anticipated products, small oligomers are present, occasionally even in excess. Apparently, they are products of reaction of monomers not fully removed in earlier stages.

The concept of step-wise controlled polyaddition method of synthesis of polyurethanes was developed in order to verify the possibility of obtaining advantageous mechanical and thermal properties of urethane elastomers. That expectation creates from the fact that the components of low polydispersity easier form regular structures in domains and thus facilitate micro-phase separation of rigid urethane-isocyanate and flexible urethane-polyol segments. This may lead to creation of phases noticeably separated so that two glass transition temperatures are observed. We have therefore recorded DSC curves for elastomer samples obtained by cross-linking the oligomers with typical chain extenders, triethylamine and aromatic triisocyanate for isocyanate- and hydroxy-terminated oligomers, respectively.

The results are presented in Figs. 11 and 12. In the thermogramme 11 one can clearly see two or even three glass transition ranges. This may suggest that the phase separation did take place in the polymers. In the curve 12 one can see just one glass transition region, but also an endothermic peak at 35.5 °C is present suggesting formation of a crystalline parts. These facts, however, and their interpretation require more studies, including mechanical testing, and will be the subject of a separate report. The properties of prepolymers synthesized in this work will be compared with their analogues prepared from the same monomers in the traditional way.

4. Summary

The study described in this paper confirmed the possibility, outlined in the previous paper [1], of preparing oligomers with controlled molecular weight distribution and terminated either with isocyanate or hydroxyl groups from typical POG and TDI in bulk.

The prepolymers can be used as precursors to be extended with trifunctional compounds. Because of regular structure and well controlled chemical composition, the extended polymers are elastomeric materials.

Moreover, as it is well known, hydroxy-terminated urethane oligomers may form stable emulsions in water. This direction of studies is also worth exploring and could result in a practical application of the controlled polyaddition of diisocyanates and diols.

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