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New route to oligocarbonate diols suitable for the synthesis of polyurethane elastomers

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Abstract

Oligo(trimethylene carbonate) and oligo(neopentyl carbonate) diols were obtained by the polymerisation of corresponding six-membered cyclic carbonates in the presence of catalysts prepared in the reaction of water with diethylzinc or triethylaluminium. Their structures were proven by means of MALDI TOF and NMR spectroscopic studies. The oligocarbonate diols were reacted with 4,4′-methylenebis(phenyl isocyanate) in the presence of 1,4-butanediol as the chain extender to obtain polyurethane elastomers. The physical and mechanical properties and hydrolytic stability of novel polyurethane elastomers were compared with those of conventional materials based on polyester type soft segments. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Six-membered cyclic carbonate; Ring-opening polymerisation; Polycarbonate diols

1. Introduction

There is current interest in the synthesis of low-molecular weight polycarbonates, terminated from both sides by hydroxyl groups, with respect to their potential applications as soft segments in polyurethane elastomers. The main advantage of polyurethanes containing oligocarbonate units is their higher hydrolytic stability than that of conventional polyester-based polyurethanes. One of the reasons for this is that the hydrolysis of carbonate linkages does not produce the acidic groups which catalyse the hydrolytic degradation of ester bonds [1–6].

The polycarbonate diols are usually obtained either by polycondensation of phosgene with diols or transesterification of five-membered cyclic carbonates with diols. This latter reaction is accompanied by decarboxylation which gives rise to poly(ether-*co*-carbonate) diols containing less then 50 mol% of carbonate units [7–12].

We reported previously that the diols of molecular weights in the range of several thousands containing more than 95% of carbonate linkages can be prepared by glycolysis of high-molecular weight poly(propylene carbonate) in the presence of titanium alkoxides as catalysts [13,14].

In the present paper, we describe a new effective method of polycarbonate diols synthesis. It involves the ring opening polymerisation of trimethylene carbonate (TMC) and 2,2-dimethyl carbonate (neopentyl carbonate, NPC) in the presence of zinc or aluminium coordination catalysts of Vandenberg type. The work deals also with the synthesis of polyurethane elastomers from the polycarbonate precursors obtained and with preliminary studies on their hydrolytical stability and mechanical properties.

2. Experimental

2.1. Materials

Diethyl carbonate, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol (neopentyl glycol), 1,4-butanediol (all from Aldrich Chem. Co) were purified according to standard methods [15]. Triethylaluminium ($AlEt_3$) (Aldrich Chem. Co), diethylzinc ($ZnEt_2$) (Aldrich Chem. Co), dibutyltin dilaurate (Fluka), stannous 2-ethyl-hexanoate (from Laboratory of Technological Processes of Warsaw University of Technology, Poland), 4,4′-methylenebis(phenyl isocyanate) (MDI) (Aldrich Chem. Co), dihydroxy(polyethylene adipate) (Purate) (Interrokita, Poland) were used without further purification.

Six-membered cyclic carbonates such as trimethylene carbonate and neopentyl carbonate were synthesised according to procedures described in the literature [16,17].

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Table 1
Polymerisation of trimethylene carbonate, TMC (reaction conditions (see Section 2); catalyst: prepared from 2 mmol of alkylmetal compound; toluene: 10 ml; TMC: 5.1 g (50 mmol))

Run no.	Catalyst (mole ratio)	Reaction			Oligo(trimethylene carbonate) diol				
		Temp. (°C)	Time (h)	Yield (%)	M_n[a] (g/mol)	M_w[a] (g/mol)	M_w/M_n	L_{OH} (–)[b]	X[c] (%)
1.	$ZnEt_2/H_2O$ (1:1)	40	20	29					
2.		60	10	24					
3.		60	20	54					
4.		80	5	45					
5.		80	10	63					
6.		80	20	72	1300	1700	1.31	84(1300)	3
7.	$AlEt_3/H_2O$ (1:1)	40	20	79	1100	1400	1.27		0
8.		60	10	49					
9.		60	20	64					
10.		80	5	68					
11.		80	10	78	1400	1900	1.36		2
12.		80	20	98	1700	2700	1.59	63 (1800)	4
13.	$AlEt_3/H_2O$ (1:0.5)	60	20	69	1600	2600	1.63		2
14.		80	5	68					
15.		80	20	84	1800	2800	1.56	67 (1700)	3
16.	$AlEt_3/H_2O$ (1:2)	60	20	70	1600	2200	1.38		1
17.		80	5	59					
18.		80	20	81	1800	2800	1.56	55 (2000)	2

[a] Molecular weight determined from GPC.

[b] Theoretical M_n calculated from L_{OH}.

[c] Content of ether units calculated from ^{1}H NMR.

2.2. Synthesis of six-membered cyclic carbonate

Trimethylene carbonate (TMC) was obtained with diethyl carbonate (240 g, 2 mol) and 1,3-propanediol (152 g, 2 mol) in the presence stannous 2-ethyl-hexanoate (19 g 0.1 mol) as a catalyst. The reagents were allowed to reflux for 8 h at 160°C and the mixture was allowed to cool down after the removal of ethanol. The obtained poly(trimethylene carbonate) was thermally depolymerised and the product of its depolymerisation was next distilled under vacuum. The crude product was recrystallised in a mixture of benzene and hexane (1:2 v/v). The resulting white crystals were dried under reduced pressure (10 mm Hg) at room temperature.

Neopentyl carbonate (2,2-dimethyltrimethylene carbonate) (NPC) was obtained analogously using diethyl carbonate (240 g, 2 mol), neopentyl glycol (208 g, 2 mol) and stannous 2-ethyl-hexanoate (19 g, 0.1 mol).

2.3. Synthesis of catalysts

The catalysts were prepared in nitrogen atmosphere at room temperature immediately before each reaction. To a glass vessel equipped with a stirrer containing 2 mmol of metal alkyl compound (diethylzinc or triethylaluminium) in 4 ml of 1,4-dioxane, the required amount of water in 4 ml of 1,4-dioxane was added drop-wise. The content of the flask was vigorously stirred. After the addition was completed, the content of the vessel was stirred vigorously until ethane evolution ceased. The volume of ethane evolved was measured in a gas burette [18].

2.4. Polymerisation procedure

The prepared solution of catalyst (8 ml) and 50 mmol of respective six-membered cyclic carbonate and toluene as a reaction medium (10 ml) were placed in a 60-ml stainless steel autoclave. The reaction vessel was then kept standing in a thermostated oil bath for the required time. Then, the products were dissolved in methylene chloride and the obtained solution was washed with dilute hydrochloric acid and water. The wash off was continued to remove fully any unreacted monomer.

The resulting oligomers, oligo(trimethylene carbonate) diol (TMCD) and oligo(neopentyl carbonate) diol (NPCD), were used for the synthesis of polyurethanes.

The polymerion of six-membered cyclic carbonates in a larger scale was led analogously in a 250-ml stainless steel autoclave using the following amount of reagents: 500 mmol of cyclic carbonate, 10 mmol of catalyst in 1,4-dioxane (40 ml), and toluene (100 ml).

2.5. Synthesis of polyurethane elastomers

Polyurethanes were prepared by using a one step bulk polymerisation procedure. Before reaction all reactants e.g. MDI, Purate, polycarbonate diols (e.g. TMCD and NPCD) and 1,4-butanediol were dried for 1 h at 70°C.

Table 2
Polymerisation of neopentyl carbonate, NPC (reaction condition (see Section 2); catalyst: prepared from 2 mmol of metal alkyl compound; toluene: 10 ml; NPC: 6.5 g (50 mmol))

Run no.	Catalyst (mole ratio)	Reaction			Oligo(neopentyl carbonate) diol				
		Temp. (°C)	Time (h)	Yield (%)	M_n[a] (g/mol)	M_w[a] (g/mol)	M_w/M_n	L_{OH} (–)[b]	X[c] (%)
1.	$ZnEt_2/H_2O$ (1:1)	40	20	39					
2.		60	10	20					
3.		60	20	48					
4.		80	5	47					
5.		80	10	56					
6.		80	20	65	3000 3500[d]	6300 4000[d]	2.10 1.14[d]	40 (2800)	3
7.	$AlEt_3/H_2O$ (1:1)	40	20	64	1700 2500[d]	2500 3000[d]	1.47 1.20[d]	51 (2200)	1
8.		60	10	51					
9.		60	20	60					
10.		80	5	57					
11.		80	10	65	2500 2700[d]	4200 3100[d]	1.68 1.15[d]	39 (2900)	2
12.		80	20	87	6200 2800[d]	13,900 3000[d]	2.24 1.07[d]		4
13.	$AlEt_3/H_2O$ (1:0.5)	60	20	60	8200	14,000	1.71		2
14.		80	5	66					
15.		80	20	70	1900	2400	1.26		
16.	$AlEt_3/H_2O$ (1:2)	60	20	64	4500	12,200	2.71	27 (4100)	
17.		80	10	46					
18.		80	20	73	1600	2500	1.56		4

[a] Molecular weight determined from GPC.
[b] Theoretical M_n calculated from L_{OH}.
[c] Content of ether units calculated from ^{1}H NMR.
[d] Molecular weight determined from MALDI TOF spectra.

Then the diols (1,4-butanediol, polycarbonate diol and/or Purate) were mixed at 100°C in a 150-ml three-necked flask equipped with a stirrer and thermometer. After 1 h MDI was progressively added into the reactor and content of the flask was vigorously stirred. The synthesis of polyurethane was carried out under nitrogen atmosphere. After the reaction was complete, the product was conditioned in a steel mould under vacuum at 35°C for 2 h.

The polyurethane elastomers were dissolved in DMSO and then isolated from the solution by pouring into water. Then, they were kept under vacuum at 70°C for one week.

2.6. Measurements

The polymerisation products were characterised by means of ^{1}H, ^{13}C NMR (Varian VXR 300 MHz) and IR spectroscopy (Specord 80—Carl Zeiss Jena). The NMR spectra of the polycarbonate diols or polyurethane elastomers were recorded in DMSO-d_6 or $CDCl_3$ solutions, respectively. The differential scanning calorimetry (DSC) measurements were conducted using a Perkin–Elmer Pyrris 1 apparatus—the samples were heated from −100°C to +250°C with a rate of 10°C/min.

The molecular weights of the polycarbonate diols or polyurethane elastomers were measured by gel-permeation chromatography (GPC) at 25°C in tetrahydrofuran solution (Shimadzu C-R4 Chromatopac apparatus—the column calibration was made using standard samples of monodispersed polystyrene) or by MALDI TOF mass spectroscopy (Kratos Kompact 4 mass spectrometer), respectively.

The hydroxyl number of the obtained polycarbonate diols was determined according to a known method, based on the reaction with acetic acetate [19,20].

The obtained polyurethane elastomers were extruded in the shape of threads and some mechanical properties of these polymers were determined using a calibrated Instron tensile tester (Model 4301).

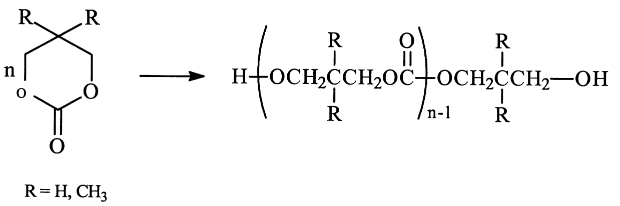
3. Results and discussion

3.1. Ring-opening polymerisation of six-membered cyclic carbonates

The polymerisation of TMC and NPC was carried out in

Fig. 1. MALDI-TOF spectrum of NPCD obtained in the neopentyl carbonate polymerisation in the presence of $ZnEt_2/H_2O$ (1:1 by mole) catalyst (Table 2, Run no. 6); tetrahydrofuran solvent.

the presence of catalysts prepared by mixing water with either diethylzinc at molar ratio 1:1 or with triethylaluminium at molar ratios 0.5:1, 1:1, and 2:1. The metal to monomer molar ratio was 0.04, a mixture of dioxane with toluene was used as the solvent and the reaction temperature was changed over the 40–80°C range (Tables 1 and 2). Under these conditions both cyclic monomers appear to undergo ring-opening polymerisations affording low-molecular weight polycarbonates terminated by hydroxyl chain-end groups.



Figs. 1 and 2 show typical MALDI-TOF spectra of the products obtained. They reveal the sets of signals corresponding to the protonated oligomers of structures **I_A** or **I_B**. The experimentally determined monomeric unit mass and residual mass for TMC oligomers (**I_A**) were found to be 102.27 and 77.39 and those for NPC oligomers (**I_B**) 130.52 and 105.27, respectively.

The number average molecular weights determined from GPC for TMC oligomers lie in the 1100–1800 Daltons range, and the polydispersity indexes in the 1.2–1.6 range. For NPC oligomers the M_n values are 1700–8200 and M_w/M_n 1.3–2.2. The M_n values determined by the GPC method differ by 3–24% from those determined by the conventional method of terminal group analysis (Tables 1 and 2). Similar differences occur between the M_n values determined on the basis of the hydroxyl number and those obtained from MALDI TOF experiments. However, the number of these latter experiments is still too small to judge whether the MALDI TOF method can be used for quantitative determination of the end group concentration.

The chemical structures of oligocarbonates obtained were confirmed by means of ^{13}C and ^{1}H NMR studies. Fig. 3 shows a typical ^{13}C NMR spectrum of poly(neopentyl carbonate) diol (**I_B**) formed in the systems studied. It reveals all signals expected for carbon nuclides in carbonate units and terminal CH_2OH groups at $\delta = 155.3$ [$CH_2(CH_3)_2CH_2O\mathit{C}(O)O$], 72.4 [$CH_2C(CH_3)_2\mathit{C}H_2OC(O)O$], 67.9 ($\mathit{C}H_2OH$), 35.1 [$CH_2\mathit{C}(CH_3)_2CH_2$], 21.3 [$C(\mathit{C}H_3)_2$] ppm. The signals observed in ^{13}C NMR spectra of poly(trimethylene carbonate) diols (**I_A**) can be attributed to the following units: 155.7 [$O\mathit{C}(O)O$], 67.9 [$\mathit{C}H_2OH$], 64.2 [$\mathit{C}H_2CH_2\mathit{C}H_2OC(O)$], 27.9 [$CH_2\mathit{C}H_2CH_2OC(O)O$] ppm.

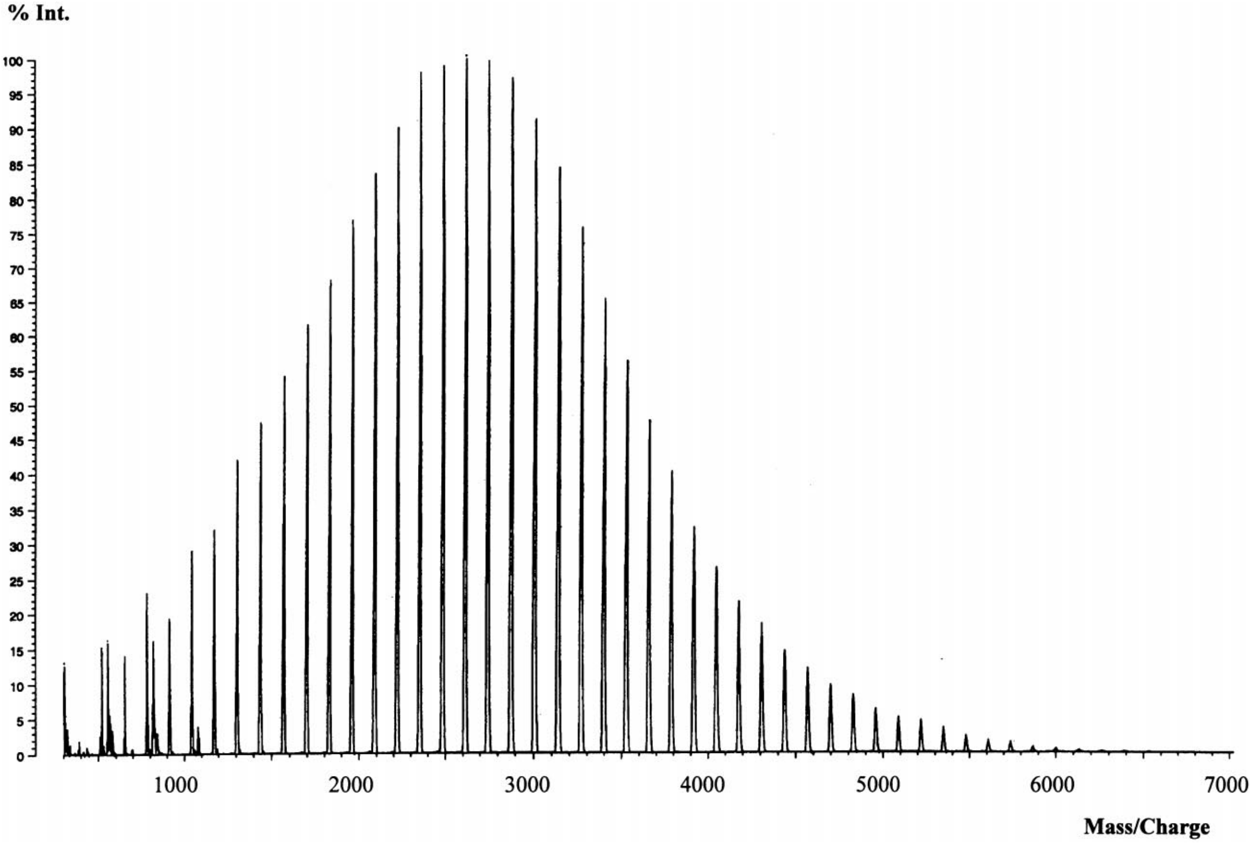
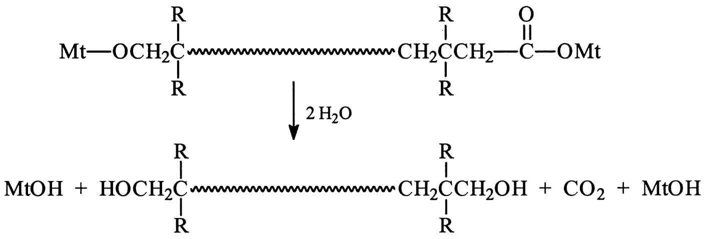


Fig. 2. MALDI-TOF spectrum of TMCD obtained in trimethylene carbonate polymerisation in the presence of $AlEt_3/H_2O$ (1:1 by mole) catalyst (Table 3, Run no. 1); tetrahydrofuran solvent.

In ^1H NMR spectra of $\mathbf{I_B}$ diols (Fig. 4), the main signals characteristic for repeating and terminal units appear at $\delta =$ 0.98 [CH_3, singlet], 3.34 [CH_2OH, triplet], 3.94 [$CH_2OC(O)O$, singlet] ppm and in spectra of ($\mathbf{I_A}$) at $\delta =$ 2.00 [$CH_2CH_2CH_2$,quintet], 3.65 [CH_2OH, triplet], and 4.18 [$CH_2OC(O)O$, singlet].

In some spectra also some small additional signals were observed characteristic for ether-type linkages at $\delta = 3.52$ [$CH_2CH_2CH_2O$, triplet] and 1.86 [$CH_2CH_2CH_2$, quintet] or 3.66 [$CH_2C(CH_3)_2CH_2O$]. However, on the basis of the intensity of these signals it can be estimated that the content of ether type bonds does not exceed 4 mol% (Tables 1 and 2). Therefore, it can be expected that carbon dioxide elimination from the polymer chain occurs practically only from terminal units during the hydrolysis of metal carboxylates, which leads to the formation of hydroxyl groups.



$$Mt{-}OCH_2\overset{R}{\underset{R}{C}}\sim\sim\sim CH_2\overset{R}{\underset{R}{C}}CH_2{-}\overset{O}{\overset{\|}{C}}{-}OMt \xrightarrow{2\,H_2O} MtOH + HOCH_2\overset{R}{\underset{R}{C}}\sim\sim\sim CH_2\overset{R}{\underset{R}{C}}CH_2OH + CO_2 + MtOH$$

A plausible explanation is that the second hydroxyl group is formed after the hydrolysis of alkoxide type active species. However, the polymerisation mechanism in these systems has not been studied yet.

As can be seen from Tables 1 and 2, the polymerisation yield increases with increasing the reaction temperature and time. The aluminium based catalysts proved to be more effective than the zinc one and enabled to obtain poly(trimethylene carbonate) and poly(neopentyl carbonate) diols in a yield of 85–95%. Similar trends were observed during preliminary scale-up experiments (Table 3). The diols prepared on a larger scale were characterised by a relatively low polydispersity index of 1.12–1.27 and their average number molecular weight was in the range of 2600–3600.

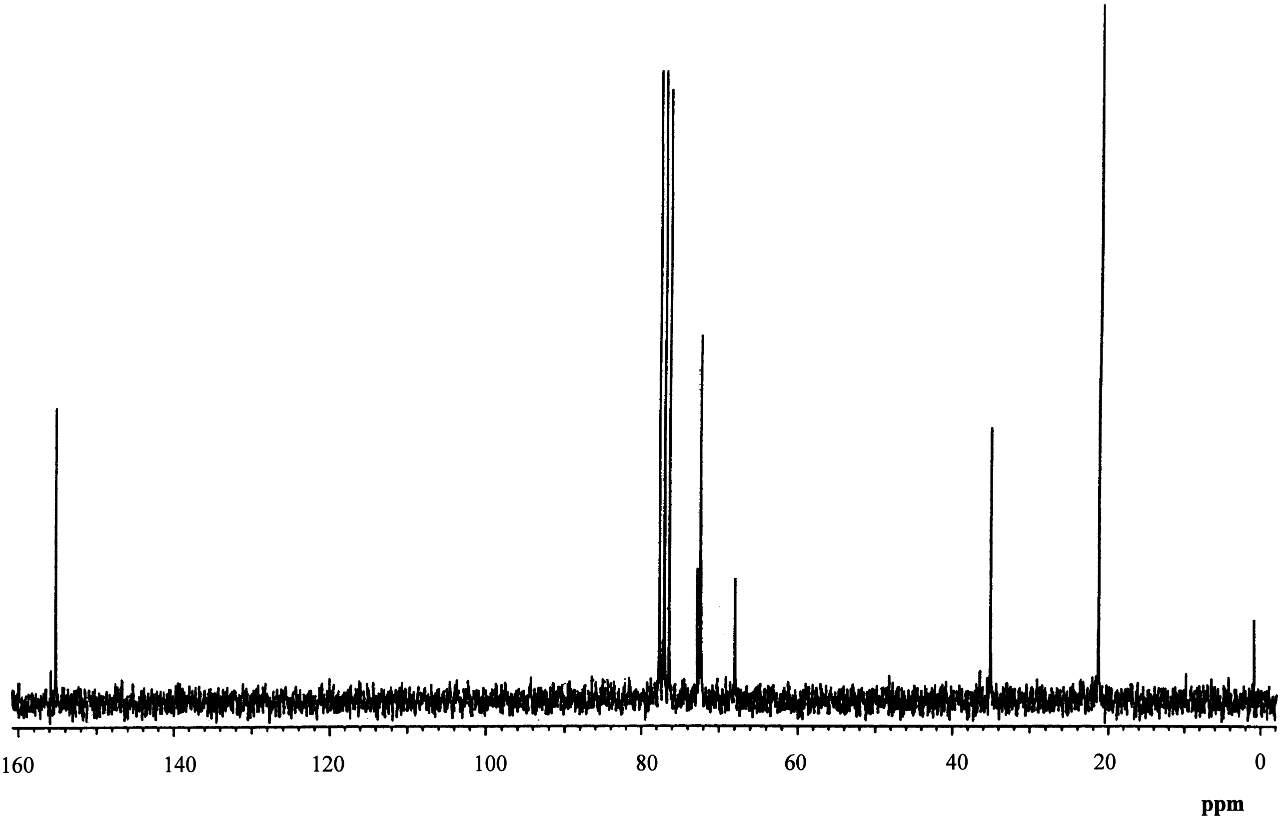


Fig. 3. ^{13}C NMR spectrum of NPCD obtained with $AlEt_3/H_2O$ (1:1 by mole) catalyst (Table 2, Run no. 11); $CDCl_3$ solvent.

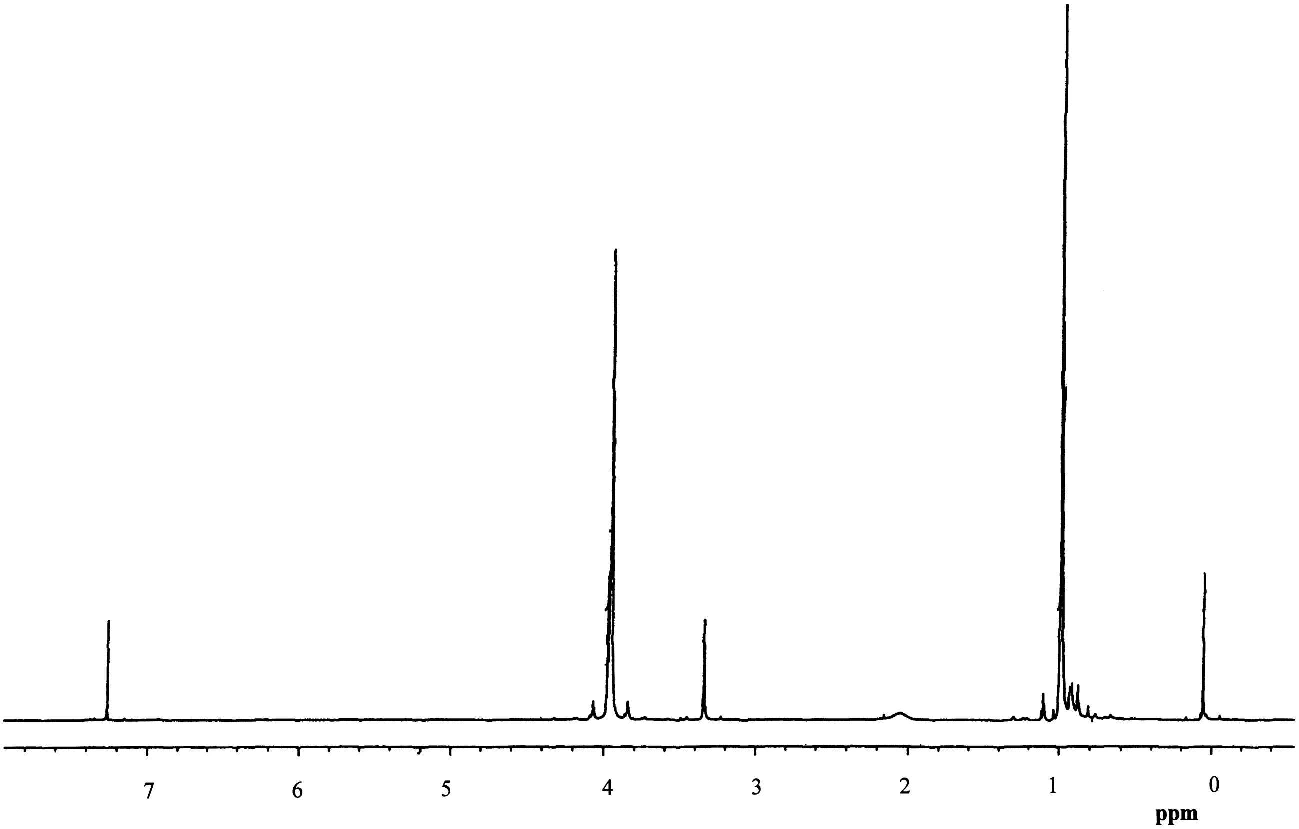


Fig. 4. ^{1}H NMR spectrum of NPCD obtained with $AlEt_3/H_2O$ (1:1 by mole) catalyst (Table 2, Run no. 11); $CDCl_3$ solvent.

Table 3
Polymerisation of trimethylene carbonate (TMC) and neopentyl carbonate (NPC) in a larger scale (reaction conditions (see Section 2); catalyst: prepared from 10 mmol of alkylmetal compound; toluene: 100 ml, NPC: 51 g (0.5 mol); TMC: 65 g (0.5 mol))

Run no.	Catalyst (mole ratio)	Reaction condition			Oligo(alkylene carbonate) diol				
		Monomer	Temp. (°C)	Time (h)	Yield (%)	M_n[a] (g/mol)	M_w[a] (g/mol)	M_w/M_n	L_{OH} (–)[b]
1	$AlEt_3/H_2O$ (1:1)	TMC	80	20	87	3200	3700	1.16	31 (3600)
2	$AlEt_3/H_2O$ (1:0.5)	TMC	80	20	95	2600	2900	1.12	53 (2100)
3	$ZnEt_2/H_2O$ (1:1)	TMC	80	20	69	3400	4000	1.18	34 (3300)
4	$AlEt_3/H_2O$ (1:1)	NPC	40	20	42	2600	3300	1.27	40 (2800)
5	$AlEt_3/H_2O$ (1:1)	NPC	80	20	86	3600	4100	1.14	29 (3900)
6	$ZnEt_2/H_2O$ (1:1)	NPC	80	20	55	3100	3700	1.19	41 (2700)

[a] Molecular weight determined from GPC.
[b] Theoretical M_n calculated from L_{OH}.

3.2. Synthesis and properties of polyurethane elastomers

4,4′-Methylenebis(phenyl isocyanate) (MDI) and 1,4-butanodiol as a chain extender were used in all the reactions of polyurethane synthesis for the synthesis of hard segments. Poly(trimethylene carbonate) diol of $M_n = 2600$ (Table 3, Run No. 2), poly(neopentyl carbonate) diol of $M_n = 3600$ (Table 3, Run No. 5) and commercially available dihydroxy-poly(ethylene adipate) (PEA) of $M_n = 2000$ were used as precursors of soft segments. The MDI:1,4-butanediol:oligodiol molar ratio was always 2.5:1.5:1, which corresponds to the so called isocyanate index equal 1. Stannous 2-ethyl-hexaonate or dibutyltin dilaurate were the polyaddition catalysts. The reaction conditions and

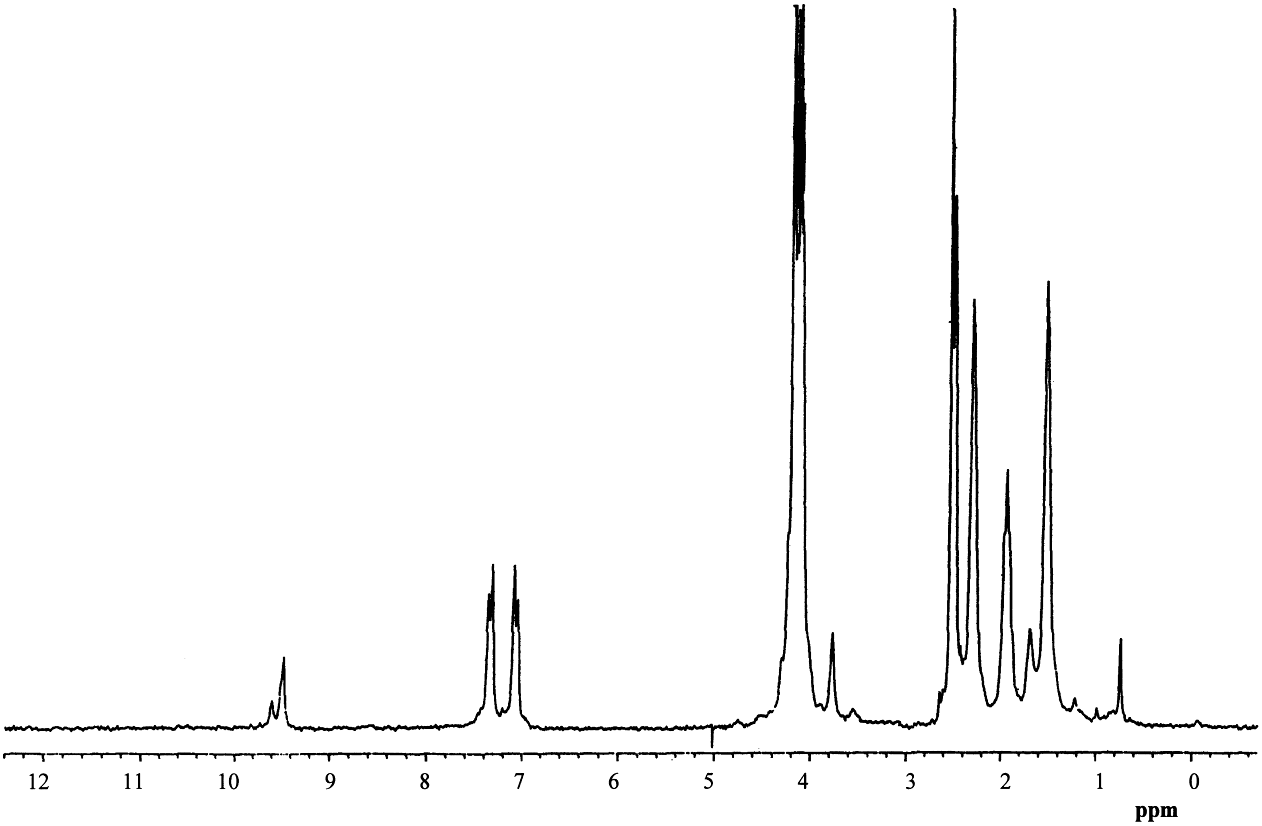


Fig. 5. ^1H NMR spectrum of polyurethane elastomer based on TMCO/Purate mixture and MDI (Table 4, Run no. 9); DMSO-d_6 solvent at room temperature.

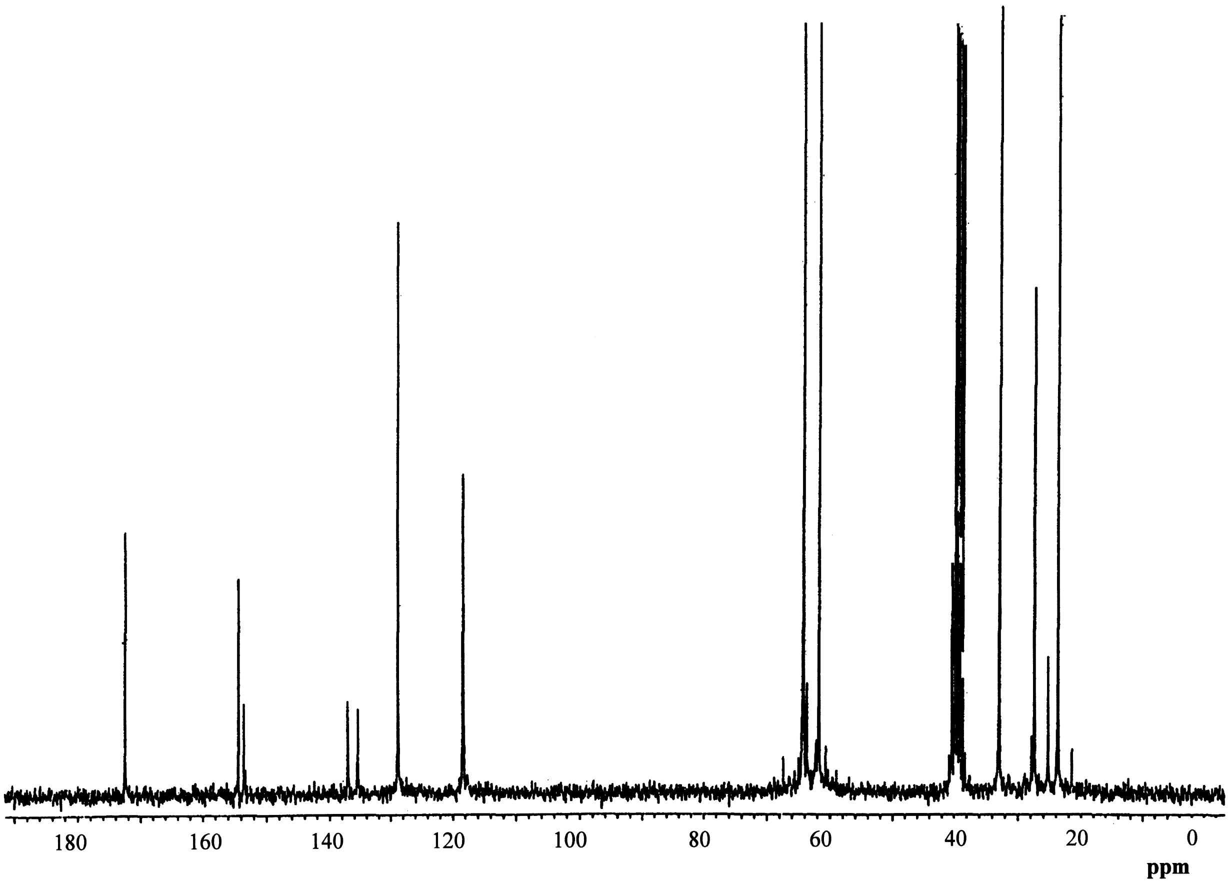


Fig. 6. ^{13}C NMR spectrum of polyurethane elastomer based on TMCO/Purate mixture and MDI (Table 4, Run no. 9); DMSO-d_6 solvent at room temperature.

molecular weight of the products obtained are listed in Table 4. It can be observed that both polycarbonate diols underwent polyaddition affording polyurethanes of M_n in the range of 18–42.9 × 10^3 g/mol and polydispersity 1.68–3.67 as determined by GPC calibrated with polystyrene standards. They formed also high-molecular weight materials in mixed system containing both polyester and polycarbonate diols. The degree of polyaddition depended on

Table 4
Synthesis of polyurethane elastomers based on 4,4′-methylenebis(phenyl isocyanate) (MDI) and oligo(trimethylene carbonate) diol (TMCD) or oligo(neopentyl carbonate) diol (NPCD)(amount of components—MDI: 6.3 g (0.025 mol); 1,4-butanodiol: 1.4 g (0.015 mol); catalyst: 0.0001 mol; TMCD: M_w = 2900 g/mol, L_{OH} = 45; NPCD: M_w = 4100 g/mol, L_{OH} = 30; Purate: dihydroxy(polyethylene adipate): M_w = 2000 g/mol, L_{OH} = 56; (2-EtHe)$_2$Sn: stannous 2-ethyl-hexanoate; DlDbSn, dibutyltin dilaurate; Isocyanate index: $I_{NCO} \approx 1$ (2% excess of MDI was used); Mole ratio: MDI:1,4-butanodiol:TMCD/NPCD/Purate = 2.5:1.5:1; (for reaction conditions see Section 2))

Run no.	Reaction components				Polyurethane elastomer			
	Purate (mol)	TMCD (mol)	NPCD (mol)	Catalyst	M_n[a] (g/mol)	M_w[a] (g/mol)	M_w/M_n	Y[b] (%)
1.	0.01			(2-EtHe)$_2$Sn	14,600	25,000	1.71	73
2.		0.01		(2-EtHe)$_2$Sn	18,000	30,200	1.68	78
3.			0.01	(2-EtHe)$_2$Sn	23,500	66,300	2.82	83
4.	0.006	0.004		(2-EtHe)$_2$Sn	17,400	63,900	3.67	76
5.	0.006		0.004	(2-EtHe)$_2$Sn	21,100	57,000	2.70	80
6.	0.01			DlDbSn	36,800	66,600	1.81	73
7.		0.01		DlDbSn	24,300	41,100	1.69	78
8.			0.01	DlDbSn	42,900	111,100	2.59	83
9.	0006	0.004		DlDbSn	19,200	37,200	1.94	76
10.	0.006		0.004	DlDbSn	32,500	103,000	3.17	80

[a] Molecular weight determined from GPC.

[b] Content of soft segment in polyurethane elastomer.

Table 5
^{1}H NMR Structural assignments of obtained polyurethane elastomers (spectrum recorded in dimethylsulphoxide-d$_6$ at room temperature)

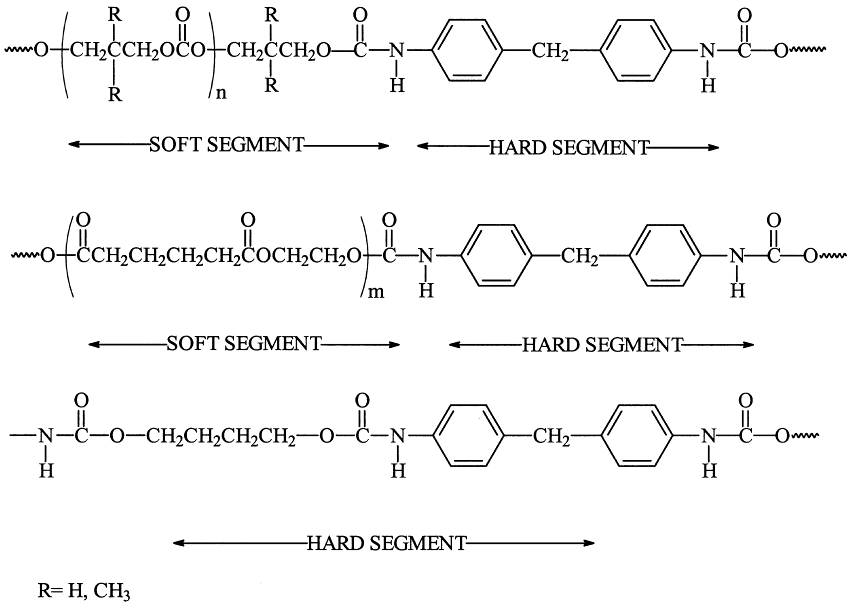
Chemical shift in ppm	Structural assignments
9.48	$\mathrm{-O(O)CNHArCH_2ArN}\mathit{H}\mathrm{C(O)O-}$
7.31	Hydrogen atoms attached to aromatic carbon at position 3
7.08	Hydrogen atoms attached to aromatic carbon at position 2
4.15	$\mathrm{-OC}\mathit{H}_2\mathrm{CH_2C}\mathit{H}_2\mathrm{O-}$
4.09	$\mathrm{-OC}\mathit{H}_2\mathrm{CH_2CH_2CH_2OC(O)NHAr-}$
3.90	$\mathrm{-OC}\mathit{H}_2\mathrm{C(CH_3)_2C}\mathit{H}_2\mathrm{O-}$
3.77	$\mathrm{-O(O)CNHArC}\mathit{H}_2\mathrm{ArNHC(O)O-}$
4.19	$\mathrm{-OCH_2CH_2CH_2CH_2C(O)OCH_2C}\mathit{H}_2\mathrm{OC(O)NHAr-}$
2.29	$\mathrm{-OCH_2CH_2CH_2C}\mathit{H}_2\mathrm{C(O)OCH_2CH_2OC(O)NHAr-}$
1.93	$\mathrm{-OCH_2C}\mathit{H}_2\mathrm{CH_2O-}$
1.51	$\mathrm{-OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2OC(O)NHAr-}$ $\mathrm{-OC(O)CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2C(O)OCH_2CH_2-}$
0.98	$\mathrm{-OCH_2C(C}\mathit{H}_3\mathrm{)_2CH_2O-}$

Table 6
^{13}C NMR Structural assignments of obtained polyurethane elastomers (spectrum recorded in dimethylsulphoxide-d$_6$ at room temperature)

Chemical shift in ppm	Structural assignments
172.5	$\mathrm{-O}\mathit{C}\mathrm{(O)-}$
154.4	$\mathrm{-CH_2CH_2CH_2O}\mathit{C}\mathrm{(O)O-}$
153.6	$\mathrm{-OCH_2CH_2CH_2CH_2O}\mathit{C}\mathrm{(O)NHAr-}$
153.3	$\mathrm{-OCH_2CH_2CH_2CH_2C(O)OCH_2CH_2O}\mathit{C}\mathrm{(O)NHAr-}$
137.1	Aromatic carbon atoms at position 1 (bonded with the methylene group)
135.4	Aromatic carbon atoms at position 4 (bonded with the urethane group)
128.8	Aromatic carbon atoms at position 2
118.3	Aromatic carbon atoms at position 3
72.1	$\mathrm{-O}\mathit{C}\mathrm{H_2C(CH_3)_2}\mathit{C}\mathrm{H_2O-}$
64.2	$\mathrm{-O}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2O-}$
63.7	$\mathrm{-OCH_2CH_2CH_2}\mathit{C}\mathrm{H_2OC(O)NHAr-}$
61.8	$\mathrm{-OCH_2CH_2CH_2CH_2C(O)OCH_2}\mathit{C}\mathrm{H_2OC(O)NHAr-}$
40.3	$\mathrm{-O(O)CNHAr}\mathit{C}\mathrm{H_2ArNHC(O)O-}$
34.9	$\mathrm{-OCH_2}\mathit{C}\mathrm{(CH_3)_2CH_2O-}$
32.9	$\mathrm{-O(O)C}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2C(O)O-}$
27.5	$\mathrm{-OCH_2}\mathit{C}\mathrm{H_2CH_2O-}$
25.3	$\mathrm{-OCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2OC(O)NHAr-}$
23.7	$\mathrm{-OCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2C(O)OCH_2CH_2OC(O)NHAr-}$
20.9	$\mathrm{-OCH_2C(}\mathit{C}\mathrm{H_3)_2CH_2O-}$

the kind of catalyst used and in all the systems studied, the polyurethanes obtained in the presence of dibutyltin dilaurate were characterised by higher molecular weights than those prepared using stannous 2-ethylhexanoate.

The ^{1}H NMR, ^{13}C NMR and IR spectra (see e.g. Figs. 5 and 6) exhibit signals characteristic for linear polyurethanes (assignments are given in Tables 5, 6 and 7) without any indication of the allophanate or the biuret linkages formation. Therefore, the structures of soft and hard segments in the polyurethanes obtained can be represented by the scheme:



Some physical and mechanical properties like glass transition temperature, melting point, fail stress, stress at 100% elongation at break of polyester-, polycarbonate- and poly(ester-*co*-carbonate)-urethanes obtained are presented in Table 8. The T_g values lie in the −8 to −5°C range and melting points of crystalline phases in the 55–89°C range. It can be noticed that the presence of carbonate segments, and especially of neopentyl derivatives causes a clear rise of the melting point T_m and decrease of the elongation at break value. Polyurethanes containing oligo(neopentyl carbonate) units are characterised also by the lowest fail stress values. The differences in tensile strength of polyurethanes comprising polyester and poly(trimethyl carbonate) groups are small and the highest fail stress

Table 7
The main absorption bands of obtained polyurethane elastomers (spectrum recorded in a KBr pellet)

Wave number in cm^{-1}	Group and band
3340	N–H in urethane group
2960	C–H in $-CH_2-$ group
2880	C–H in $-CH_3$ group
1740	$-C{=}O$ in carbonate group
1750–1690	$-C{=}O$ in urethane group
1600	C–H in $-C_6H_4$
1250	C–O in –C(O)O– group

values were observed for elastomers comprising a mixture of both soft segments.

The mechanical properties of the polyurethanes obtained were studied again after storing in water for 3 weeks at 70°C. After this test, the EPURs containing only polyester type soft segments retain ca 60–68% of the original value of fail stress and 76–79 of the value of elongation at break (Table 8, samples no. 1 and 6). Changes of these parameters are clearly smaller in the case of polyurethanes containing polycarbonate segments, which confirms earlier reports of higher hydrolytic stability of these segments than that of polyester units. The polyurethanes based on oligo(trimethylene carbonate) diols or oligo(neopentyl carbonate) diols preserve ca 86–89% of their initial fail stress and 78–85% of initial elongation at break (Table 8, samples 2, 3, 7 and 8). It is interesting, however that the polyurethanes containing a mixture of poly(trimethylene carbonate) and polyester type segments (Table 8, samples no. 2 and 9) exhibit also a reasonably high hydrolytic stability, which may offer a synthetic way to elastomers of good mechanical properties and improved resistance toward hydrolysis.

4. Conclusions

The ring-opening polymerisation of six-membered cyclic carbonates like trimethylene carbonate and neopentyl carbonate in the presence of a catalyst prepared in the reaction of water with diethyl zinc or triethylaluminium seems to be an efficient method for the synthesis of low-molecular weight polycarbonates terminated from both sides by hydroxyl groups. The ether linkages content in diols obtained does not exceed 4 mol% which indicates that the propagation step occurs practically without any decarboxylation.

These preliminary studies permit us to suggest that polycarbonate diols prepared in this way may be applied for the synthesis of polyurethane elastomers of improved hydrolytic stability.

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Table 8
Mechanical properties of the obtained polyurethane elastomers based on polycarbonate diols (for synthesis of polyurethane elastomers see Section 2 and Table 4)

Polyurethane elastomer											
Sample no.[a]	T_g[c] (°C)	T_m[d] (°C)	Q_r[e] (MPa)	Q_{100}[e] (MPa)	E_r[e] (%)	After hydrolysis[b]					
						Q_r[e] (MPa)	(%)[f]	Q_{100}[e] (MPa)	(%)[f]	E_r[e] (%)	(%)[f]
1.	−8	56	18.9	3.9	670	12.9	68	2.7	69	510	76
2.	2	64	18.1	3.7	560	15.6	86	3.0	81	470	84
3.	−9	73	15.6	3.2	380	13.4	86	2.5	79	300	81
4.	2	63	20.1	4.8	580	15.7	78	4.1	85	450	76
5.	−8	78	15.7	3.5	400	12.4	79	2.7	76	340	84
6.	−6	55	22.6	4.3	720	13.5	60	3.3	77	570	79
7.	5	74	20.8	4.4	530	18.5	89	3.5	80	450	85
8.	−7	87	16.5	3.2	410	14.4	87	2.9	91	320	78
9.	−2	61	26.4	5.7	590	23.3	88	4.9	86	480	81
10.	−6	89	21.6	3.6	430	15.6	72	3.0	82	370	85

[a] See Table 4.
[c] Glass transition temperature determined from DCS.
[d] Melting point determined from DSC.
[e] Q_r: fail stress; Q_{100}: stress at 100% elongation; E_r: elongation at break.
[b] Hydrolysis test: the sample of polyurethane was heated in water at 70°C for three weeks.
[f] Percentage of initial value.

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