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Investigations on the synthesis and properties of biodegradable poly(ester-carbonate-urea-urethane)s

Magdalena M. Mazurek*, Gabriel Rokicki

Warsaw University of Technology, Department of Chemistry, Chair of Polymer Chemistry and Technology, ul. Noakowskiego 3, 00-664 Warsaw, Poland
**Corresponding author: e-mail: mmazurek@ch.pw.edu.pl*

A new method of the synthesis of oligo(tetramethylene succinate-co-carbonate) diols using dimethyl succinate, 1,4-butanediol and tetramethylene bis(methyl carbonate) was elaborated. The resultant oligomerols (M_n = 2600–3700) were characterized by FTIR, ^{1}H NMR, GPC and DSC analysis. Depending on the content of carbonate units in the polymer molecules, the melting point of the crystalline phase changes significantly. The synthesis of poly(ester-carbonate-urea-urethane)s was carried out with two aliphatic diisocyanates – cyclic IPDI or linear HDI. The resultant products exhibited very good mechanical properties – tensile strength up to 60 MPa and elongation at break about 500%. Preliminary studies confirmed that the presence of ester units in the soft segments as well as lack of crystalline phase significantly enhances the biodegradability of the PUR in comparison to that of polyurethanes based on carbonate oligomers.

Keywords: polyurethane, oligo(ester-carbonate) diol, biodegradation.

INTRODUCTION

Polyurethanes (PUR) are one of the most frequently used plastics in biomedical materials. Due to their mechanical and biological properties (unique combination of toughness, durability, flexibility, biocompatibility and biostability) they are suitable materials for use in a range of implantable medical devices. The most common oligomerols used as soft segments in the synthesis of polyurethanes are oligoestrols, oligoetherols[1, 2] and more recently oligocarbonate diols[3]. Polyurethanes based on oligoestrols such as oligo(lactid acid), oligo(glycolic acid)[4] and oligo(ε-caprolactone)[5] are susceptible to hydrolytic biodegradation, however, oligoester segments easily crystallize. The presence of crystalline structure in polyurethanes suppresses their biodegradation[6]. It is also known that aliphatic polycarbonates such as poly(tetramethylene carbonate)s exhibit a lowered tendency to crystallization but their biodegradation is suppressed. Polyurethanes based on oligocarbonate diols exhibit excellent mechanical properties such as high tensile strength (40 MPa) combined with high elongation at break (400%)[7]. Taking into account the properties of ester and carbonate diols mentioned above, we decided to synthesize the oligo(ester-carbonate) diols containing various amounts of carbonate units, and use them as soft segments in the synthesis of PUR. The ester to carbonate unit ratio determines the ability to crystallization as well as the biodegradation of PUR.

The most common method used in the synthesis of poly(ester-carbonate)s is copolymerization of cyclic esters (L-lactide, ε-caprolactone) with cyclic carbonate monomer - trimethylene carbonate (TMC)[5–7, 8, 9, 10]. Yang et al. prepared a series of new poly(ester-carbonate)s by a simple combination of polycondensation and ring-opening-polymerization (ROP) of hydroxyl terminated poly(butylene succinate) macromers and various cyclic carbonate monomers[11]. Poly(butylene carbonate-*co*-butylene succinate) with low carbonate unit content (<20 mol%), which can be used for poly(L-lactide) modification have been developed by Mitsubishi Gas Chemical Company[12]. *Candida antarctica* Lipase B (CALB) was found to catalyze condensation reactions of diethyl carbonate (DEC), respective diester, and diol to form aliphatic poly(carbonate-*co*-ester)s. Poly(butylene carbonate-*co*-butylene succinate) and poly(hexamethylene carbonate-*co*-hexamethylene adipate) with about 1:1 mol/mol ester-to-carbonate repeat units ratio, were prepared[13].

We have found only a few reports concerning poly(ester-carbonate-urethane)s. W. R. Wagner and co-workers obtained PUR based on poly(ε-caprolactone), poly(hexamethylene carbonate) and 1,4-butylene diisocyanate with putrescine as a chain extender[14]. ε-Caprolactone was also used in the copolymerization with trimethylene carbonate and neopentyl carbonate. The resultant oligomerol was used as a soft segment in the reaction with MDI and 1,4-butanediol[15]. A mixture of poly(butylene carbonate) and poly(butylene succinate) diols was used in the reaction with hexamethylene diisocyanate to obtain biodegradable multiblock polyurethane elastomers[16].

In this paper we present a new method of synthesis of biodegradable polyurethanes based on aliphatic oligo(ester-carbonate) diols. Poly(ester-carbonate-urea-urethane)s were obtained using the prepolymer method, in the reaction of oligo(tetramethylene succinate-*co*-carbonate) diols with two different aliphatic diisocyanates – cyclic IPDI or linear HDI, carried out without a catalyst. Water was used as a chain extender. The influence of carbonate units content in the soft segment on PUR properties and biodegrability was investigated and discussed.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) (98%), 1,4-butanediol (99%) (Aldrich), hexamethylene diisocyanate (HDI) (≥98%) (Fluka Analytical); titanium(IV) butoxide (Ti(OBu)4) (≥97%) (Fluka); acetonitrile (99.5%), chloroform (98.5%) (Chempur), N,N-dimethylformamide (99%), phosphate buffer pH = 7.2 (POCh); lipase from *Pseudomonas cepacia* (activity 46.2 U/mg), lipase from *Pseudomonas* sp. (activity 24.0 U/mg) (Sigma) and dimethyl succinate (98%) (Sigma-Aldrich) were used

as received. Tetramethylene bis(methyl carbonate) was obtained from 1,4-butanediol and dimethyl carbonate using the procedure reported by us earlier.[17]

Characterization techniques

^{1}H NMR spectra were recorded on a Varian VXR 400 MHz spectrometer using tetramethylsilane as an internal standard, and $CDCl_3$ or DMSO-d_6 as a solvent.

FT-IR spectra were recorded on a Bruker ALPHA-P FT-IR spectrometer operating in the spectral range of 375–4000 cm^{-1} with ATR technique and resolution of 0.9 cm^{-1}. The samples were prepared in the form of thin layers of substances applied at ATR attachment.

The mechanical properties of poly(ester-carbonate-urea-urethane)s were determined using a testing machine Instron 5566. Head speed – 100 mm/min. The samples were dog-bone shaped with 20 mm length and 1 mm thickness of the measuring segment.

DSC studies were carried out using a TA Instruments DSC Q200 apparatus. The oligo(tetramethylene succinate-*co*-carbonate) diols samples were heated in a temperature range from –60 to 100°C, then cooled backward to –60 °C and heated again to 100°C. The poly(ester-carbonate-urea-urethane)s were heated in a temperature range from –80 to 250°C and cooled backward to –80°C. Heating and cooling rate was 10°C/min in all measurements.

Molecular weight measurements were performed at 30°C using GPC Malvern Viscotek apparatus with Jordi Gel DVB Mixed Bed (250 mm x 10 mm) column. Dichloromethane as an eluent and polystyrene as a standard were used.

Hardness measurements of polyurethane films were performed using Shore durometer (A- and D-scale).

Synthesis of the oligo(tetramethylene succinate-*co*-carbonate) diols

The procedure of the tetramethylene bis(methyl carbonate) synthesis from 1,4-butanediol and dimethyl carbonate was reported by us earlier[17]. As a catalyst, $Ti(OBu)_4$ (0.005% mol/mol of diol) was used instead of potassium carbonate. Tetramethylene bis(methyl carbonate) was used as a high boiling carbonate monomer in the next step to obtain oligo(tetramethylene succinate-*co*-carbonate) diols.

In a 100 cm^3 three-neck round-bottomed flask equipped with a magnetic stirrer, thermometer, distilling condenser and nitrogen supply system, 32.37 g (0.36 mol) of 1,4-butanediol, 22.59 g (0.10 mol) of tetramethylene bis(methyl carbonate), 20.08 g (0.14 mol) of dimethyl succinate and 0.08 g (0.002 mol) of $Ti(OBu)_4$ were placed. In the first step the reaction was carried out at 150–180°C for 5 h under atmospheric pressure with a nitrogen flow, until no methanol was observed in the distillate (refractive index was measured). Then, the reaction was continued for 3 hours with gradually increasing the temperature and decreasing pressure from 20 mbar at 180°C (1 h), through 0.5 mbar at 180°C (1 h) to 0.5 mbar at 200°C (1 h). The product (ECD-57) was dissolved in chloroform and washed 3 times with 3% HCl_{aq} and then 3 times with distilled water. After solvent evaporation under the reduced pressure 34.3 g of the product was obtained as a white solid with M_n = 3750 and the carbonate units content of 57%$_{mol.}$

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 4.14 (t, $OC(O)OCH_2$), 4.09 (t, $C(O)OCH_2$), 3.65 (two overlapping triplets, CH_2O), 2.6 (t, $CH_2C(O)O$), 1.75-1.65 (m, $OCH_2C\underline{H_2}$)

ATR IR; λ (cm^{-1}): 3550 (O-H), 2960 (C-H), 1730 (C=O), 1240-1160 (C-O) cm^{-1}.

Other oligomerols with different carbonate units content were obtained according to a similar method.

Synthesis of poly(ester-carbonate-urea-urethane)s

Synthesis of urethane prepolymers

In a 100 cm^3 two-neck round-bottom flask fitted with a magnetic stirrer, thermometer and nitrogen supply system, 15.26 g (0.0041 mol) of oligo(tetramethylene succinate-*co*-carbonate) diol (ECD-57) was placed and dried under reduced pressure (0.5 bar) at 100°C for about 1 h. Then 2.59 g (0.0122 mol) of isophorone diisocyanate (IPDI) was added. The reaction was carried out (about 3 hours) under a nitrogen atmosphere at 80–85°C until the disappearance of absorption bands of OH groups in FTIR spectra. Then, the product was deaerated under reduced pressure without stirring until no air bubbles formation was observed.

Syntheses of urethane prepolymers based on HDI were performed according to the same procedure. Urethane prepolymers were colorless liquids of high viscosity.

Obtaining poly(ester-carbonate-urea-urethane) foils

11 g of urethane prepolymers were poured onto the open glass form (10 cm x 10 cm x 0.5 cm) to obtain poly(ester-carbonate-urea-urethane) foils of ca. 1 mm thickness. The process of chain extending of urethane prepolymer was performed in a climatic chamber under the controlled conditions of humidity and temperature: 1 day at 75°C under 5% of humidity, 2 days at 70°C, 10% of humidity, 1 day at 70°C, 20% of humidity and 3 days at 60°C, 40% of humidity.

Solubility test

The solubility of the obtained polyurethane films in DMF, chloroform and acetonitrile was tested. The samples were cut into small disks (of 5 mm diameter and 1 mm thickness) and placed in the flasks with 2 cm^3 of each solvent. The observations of samples' changes were performed for two days.

Biodegradation of poly(ester-carbonate-urea-urethane)s

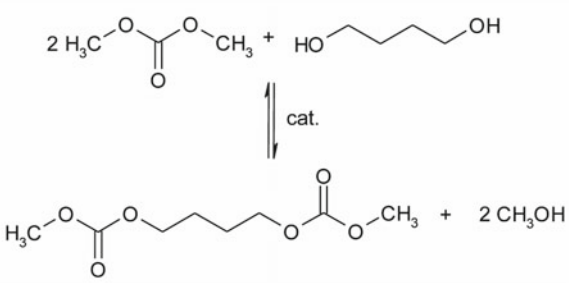
Samples (disks of 5 mm diameter and 1 mm thickness) of polyurethanes cut from the films were rinsed with ethanol and distilled water and dried in a vacuum oven, and then stored at room temperature for at least 1 week in order to approach the equilibrium crystallinity prior to use. These clean film samples with the initial weight of about 20–30 mg were incubated in vials containing 1.0 cm^3 of phosphate buffer solution (pH = 7.280), phosphate buffer pH = 7.283 with *Pseudomonas cepacia* enzyme and phosphate buffer pH = 7.287 with *Pseudomonas* sp. enzyme. The vials were sealed with PP caps with silicone/PTFE septum and transferred into a thermostated chamber at 60.0 ± 0.2°C with recipro-

cal shaking (60 rpm). After a predetermined period of incubation, the film samples were taken out and well rinsed with demineralized water, and dried to constant weight in vacuum at room temperature. The lipase-catalyzed biodegradation behavior was characterized by the weight loss of the samples. Due to a much lower content of crystalline phase, the preliminary biodegradation investigations were performed on PUR samples based on IPDI.

RESULTS AND DISCUSSION

Synthesis of oligo(tetramethylene succinate-*co*-carbonate) diols

In this study oligo(tetramethylene succinate-*co*-carbonate) diols were used as soft precursors in the polyurethane synthesis. The oligomerols were obtained in a three-step polycondensation method. In the first step tetramethylene bis(methyl carbonate) was obtained in the reaction of dimethyl carbonate (DMC) and 1,4-butanediol (Scheme 1).



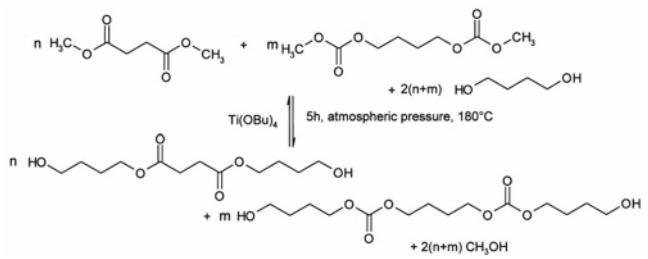
Scheme 1. Synthesis of tetramethylene bis(methyl carbonate)

It was found that the direct use of DMC as a source of carbonate linkages in the synthesis of oligo(ester--carbonate)s is inconvenient due to the formation of an azeotrope with methanol and deterioration of the monomers molar ratio. Synthesis of tetramethylene bis(methyl carbonate) was carried out using high molar excess of DMC, so the loss of carbonate monomer was not significant for the yield of the crystalline product.

In the next step the obtained tetramethylene bis(methyl carbonate) was used as a carbonate monomer in the reaction with 1,4-butanediol and dimethyl succinate to obtain oligo(tetramethylene succinate-*co*-carbonate) diols. The molar ratio of ester and carbonate monomers determined the content of carbonate units in the final product. In contrast to dimethyl carbonate, tetramethylene bis(methyl carbonate) does not form an azeotrope with methanol and the latter one can be selectively removed from the reaction mixture by distillation to maintain the intended molar ratio of ester to carbonate units.

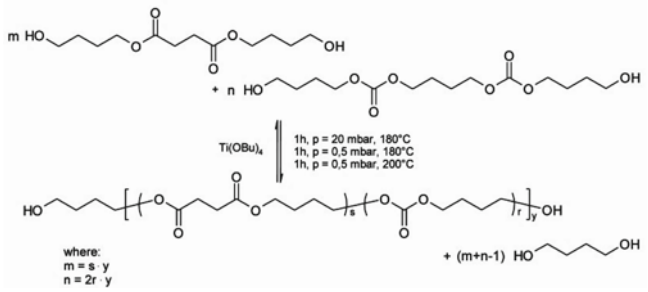
All oligo(tetramethylene succinate-*co*-carbonate) diols containing from 0 to 94 mol% of carbonate units were obtained according to the method mentioned above. The characteristics of the oligomerols are shown in Table 1.

It was found that complete removal of methyl groups from tetramethylene bis(methyl carbonate) as well as from dimethyl succinate in the alcoholysis reaction in the second step (Scheme 2) is crucial for polyurethane synthesis. This reaction should be carried out under inert gas flow without pressure reduction.



Scheme 2. Glycolysis – the second step of the synthesis of oligo(tetramethylene succinate-*co*-carbonate) diol

The final step – removing of an excess of 1,4-butanediol and the polycondensation was proceeded under the reduced pressure (20–0.5 mbar) at a temperature lower than 210°C (Scheme 3).



Scheme 3. Polycondensation – the third step of the synthesis of oligo(tetramethylene succinate-*co*-carbonate) diol

Table 1. Characteristics of oligo(tetramethylene succinate-*co*-carbonate) diols

Run	Sample	Theoretical content of carbonate units	Content of carbonate units (^{1}H NMR)[a]	M_n (^{1}H NMR)[a]	M_n (GPC)[b]
		mol.%	mol.%		
1	ED [c]	0	0	2000	2280
2	ECD-16 [d]	18	16	3480	
3	ECD-30	33	30	2935	
4	ECD-41	46	41	2670	
5	ECD-44	50	44	2730	3230
6	ECD-53	57	53	2800	3070
7	ECD-58	60	58	3750	3560
8	ECD-65	70	65	2960	3670
9	ECD-71[e]	85	71	3025	3450
10	ECD-74[e]	85	74	3430	4740
11	ECD-79	80	79	2650	3220
12	ECD-87	89	87	2990	3700
13	ECD-94	95	94	3070	

a) calculated from ^{1}H NMR spectra,
b) measured by GPC,
c) ED means oligo(tetramethylene succinate) diol,
d) ECD-16 – means: oligo(tetramethylene succinate-*co*-carbonate) diol containing 16mol.% carbonate units,
e) polycondensation was carried out at 225°C.

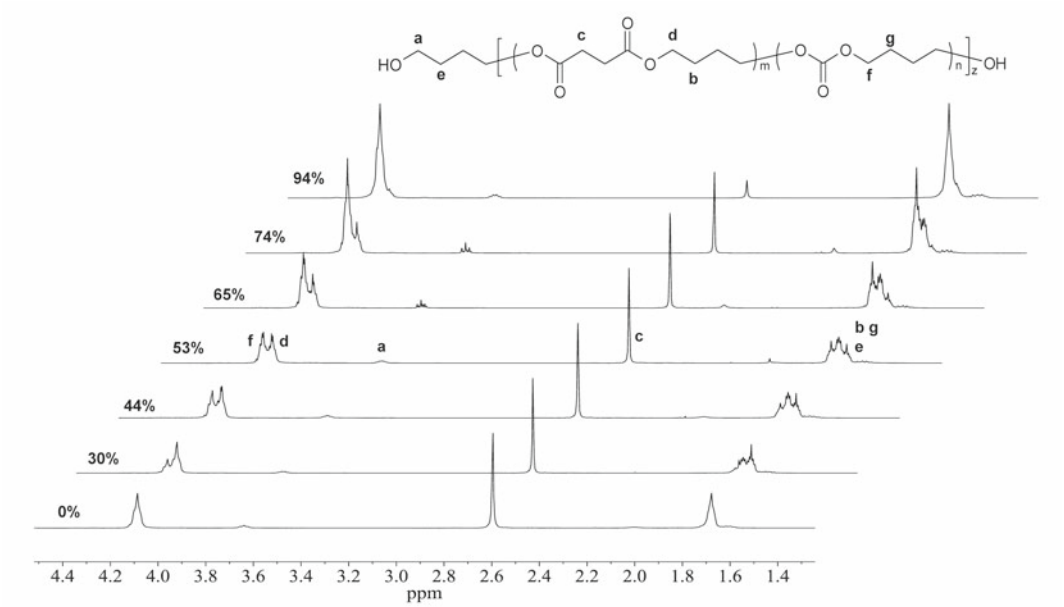


Figure 1. ^{1}H NMR ($CDCl_3$) spectra of the obtained oligo(tetramethylene succinate-*co*-carbonate) diols with different content of carbonate units

It was found that above 220°C decarboxylation takes place and lower concentration of carbonate units in the product was observed (Table 1, runs 9 and 10).

It is to underline that the titanium catalyst should be removed from the oligomerols. Its presence can deteriorate the synthesis of urethane prepolymers.

Figure 1 shows the ^{1}H NMR spectra of oligo(tetramethylene succinate-*co*-carbonate) diols containing different amount of carbonate units. Taking into account the signals intensity ratio of protons corresponding to CH_2OH (a) and $CH_2OC(O)$ (d), $CH_2OC(O)O$ (f), $CH_2C(O)O$ (c) groups, a number-average molecular weight of oligomerols was calculated (equation 1) and the molar content of carbonate units was estimated (equation 2).

$$M_n=[(f+d)-c] \cdot M_{\text{carbonate repeating unit}} + c \cdot M_{\text{ester repeating unit}} + M_{\text{diol}} \quad (1)$$

$$\text{Molar fraction of carbonate units} = \frac{(f+d)-c}{f+d} \quad (2)$$

The absence of signals characteristic for OCH_3 protons indicates that all oligomerol chains were terminated with hydroxyl groups, what is very important in case of using such oligomerols in the synthesis of polyurethanes. Monofunctional oligomers can significantly reduce the polyurethane molecular weight.

The IR analysis also confirmed the structure of the obtained oligo(tetramethylene succinate-*co*-carbonate) diols. There are absorption bands characteristic of stretching vibrations of OH groups at 3500 cm^{-1}, absorption bands characteristic of carbonyl groups of carbonate (1735 cm^{-1}) and ester (1720 cm^{-1}) linkages in the ATR IR spectrum (Fig. 2). There were no absorption bands characteristic of ether bonds in the spectra what indicates that etherification is suppressed when the polycondensation is proceeded below 210°C.

Thermal analysis of oligo(tetramethylene succinate-*co*--carbonate) diols

According to the data collected in Table 2 it can be observed that with the increasing molar content of carbonate units in oligo(tetramethylene succinate-*co*-carbonate) diols, the melting point (T_m) decreases from 98.9°C (127.5 J/g) for oligomerol with 16 mol% to 51.0°C (75.0 J/g) with 53 mol% of carbonate units. Samples containing carbonate units in the range of 53 to 74 mol% were amorphous. For oligomerols with higher amount of carbonate units (87–94 mol%) the crystalline phase was again observed (for ECD-94 T_m = 41.6°C and melting enthalpy ΔH_{mS} = 91.3 J/g). However, the highest melting point and the highest content of crystalline phase (106.1°C, 216.6 J/g) were observed for oligo(tetramethylene succinate) diol (ED).

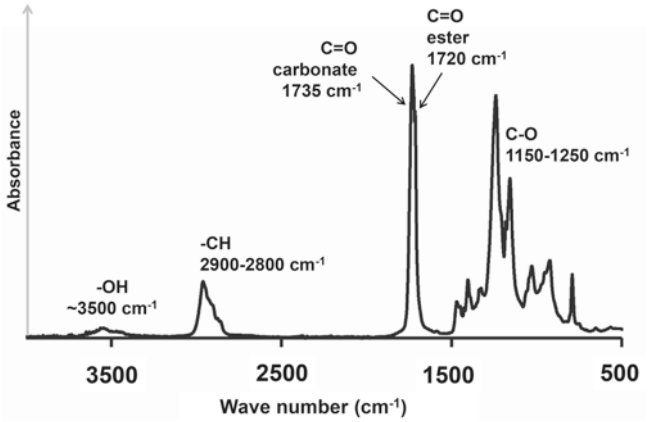


Figure 2. ATR IR spectrum of oligo(tetramethylene succinate--*co*-carbonate) diol (ECD-65)

Synthesis of poly(ester-carbonate-urea-urethane)s

Poly(ester-carbonate-urea-urethane)s were synthesized using a two-step prepolymer method in the reaction of isophorone diisocyanate (IPDI) or hexamethylene diisocyanate (HDI) with oligo(tetramethylene succinate--*co*-carbonate) diols without using catalyst and solvent. Urethane prepolymers were poured onto the open glass form and the process of chain extending was carried out using water vapour as a chain extender[17].

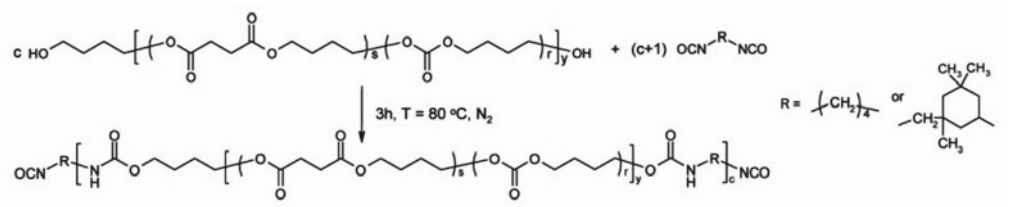
Synthesis of urethane prepolymer

In the synthesis of urethane prepolymer a threefold molar excess of diisocyanate was used. The reaction

Table 2. Thermal properties of poly(tetramethylene succinate-*co*-carbonate) diols of different carbonate units content

Run	Sample	T_m	ΔH_mS	T_g	T_c	ΔH_cS
		°C	J/g	°C	°C	J/g
1	ED [a)]	106.1	216.6	-48.6	64.9	161.6
2	ECD-16 [b)]	98.9	127.5	-42.9	58.83	131.8
3	ECD-30	76.7	87.8	-45.5	33.1	100.4
4	ECD-41	68.4	92.1	-44.6	–	–
5	ECD-44	50.3	67.4	-45.4	7.0	65.1
6	ECD-53	51.0	75.0	-46.0	–	–
7	ECD-57	–	–	-42.7	–	–
8	ECD-65	–	–	-43.9	–	–
9	ECD-71	–	–	-44.5	–	–
10	ECD-74	–	–	-42.8	–	–
11	ECD-79	33.7	2.2	-43.3	–	–
12	ECD-87	41.4	109.5	-45.5	–	–
13	ECD-94	41.6	91.3	-46.9	–	–

a) ED means oligo(tetramethylene succinate) diol,
b) ECD-16 – means: oligo(tetramethylene succinate-*co*-carbonate) diol containing 16mol.% carbonate units.



Scheme 4. Reaction of oligo(tetramethylene succinate-*co*-carbonate) diol with an excess of diisocyanate

was carried out at 80–85°C under nitrogen atmosphere (Scheme 4).

The progress of the reaction was controlled by IR spectroscopy – disappearance of absorption bands characteristic for terminal OH groups (3500 cm^{-1}) and the appearance of absorption bands characteristic of NH group (3360 cm^{-1}) of the urethane bond was monitored.

Chain extending of urethane prepolymers

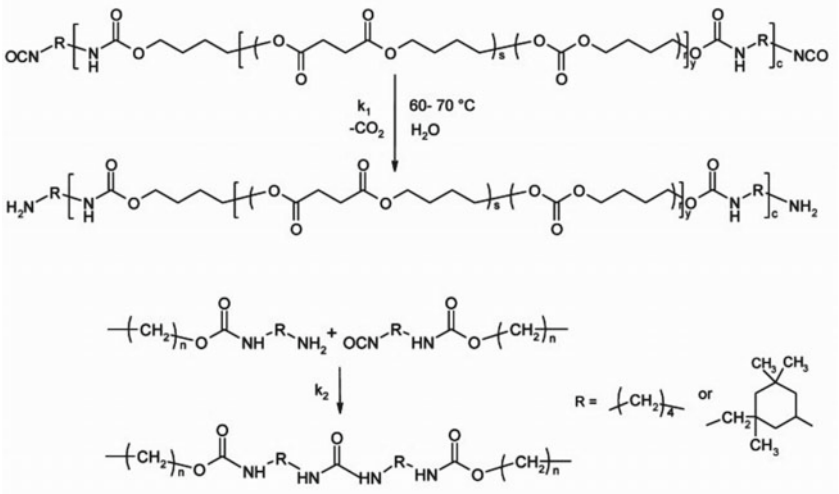
The process of obtaining poly(ester-carbonate-urea--urethane) films was proceeded in a climatic chamber using water vapor as a chain extender. Hydrolysis of the diisocyanate group (k_1 reaction rate constant) leads to an amine group, which immediately reacts with the diisocyanate group (k_2) from next molecule. As a result of a reaction between diisocyanate and amine groups, an urea bond is formed (Scheme 5). Due to the higher reaction rate of urea formation ($k_1 << k_2$), stoichiometry of the reaction can be precisely controlled and poly(urea--urethane) of high molecular weight can be obtained.

The chemical structure of resultant poly(ester-carbonate-urea-urethane)s was confirmed by ^{1}H NMR spectroscopy (Fig. 3). In the spectrum a doublet (r) at 2.7 ppm corresponding to the protons of CH_2 groups neighboring to the urea bond, triplet (y) 3.9 ppm corresponding to protons of the CH_2 groups in the direct vicinity of urethane groups, triplet (h) at 7.0 ppm chemical shift originating from urea protons and a doublet (i) at 7.1 ppm corresponding to urethane protons can be observed. There were no signals corresponding to protons of CH_2 or CH groups located adjacent to NCO groups, which proves a complete conversion of isocyanate groups.

A complete conversion of NCO groups was also confirmed by ATR IR analysis (Fig. 4). There were no absorption bands characteristic of NCO (2250 cm^{-1}) and OH (3500 cm^1) groups in the IR spectra.

Solubility of poly(ester-carbonate-urea-urethane)s

It was observed that only PURs obtained in the reaction of ECDs of high molecular weight (above 3000) with IPDI were soluble in the selected solvents (chloroform,



Scheme 5. Synthesis of poly(ester-carbonate-urea-urethane)

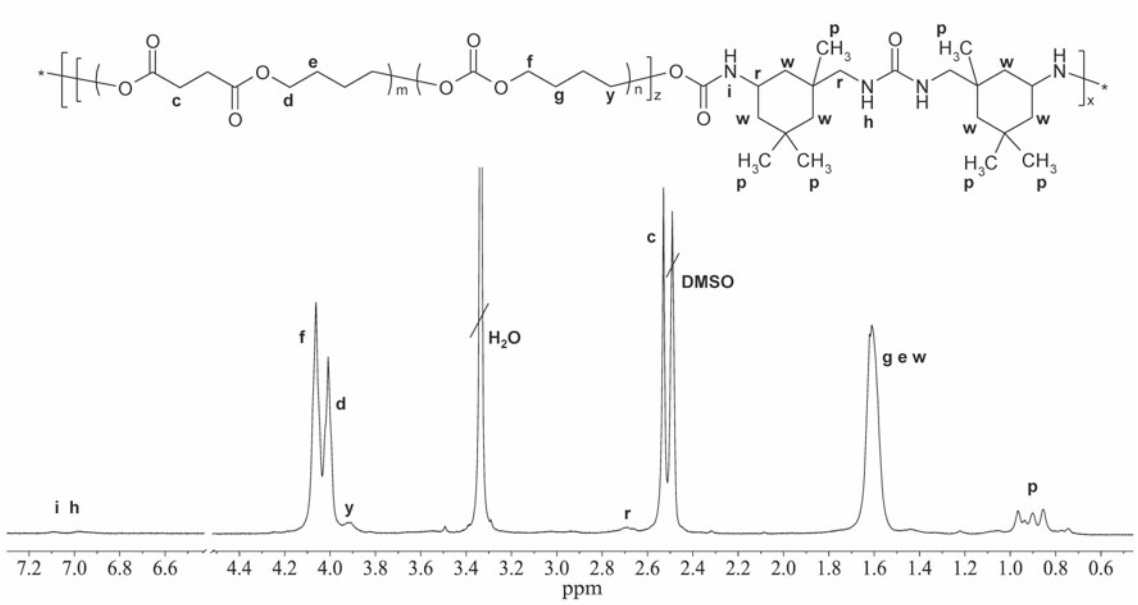


Figure 3. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of poly(ester-carbonate-urea-urethane) obtained from ECD-57 and isophorone diisocyanate

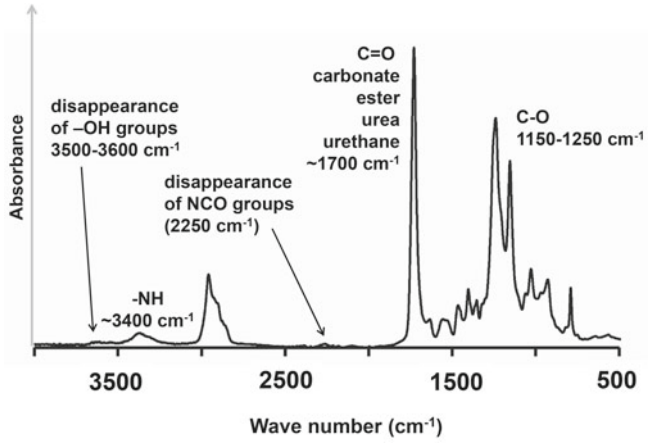


Figure 4. ATR IR spectrum of poly(ester-carbonate-urea-urethane) obtained from ECD-57 and IPDI

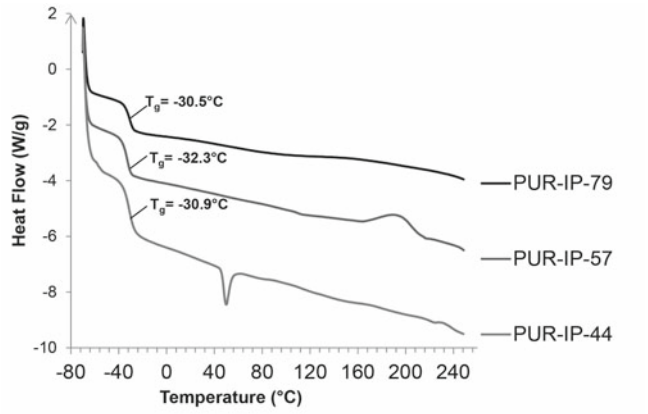


Figure 5. DSC curves of poly(ester-carbonate-urea-urethane)s obtained from HDI

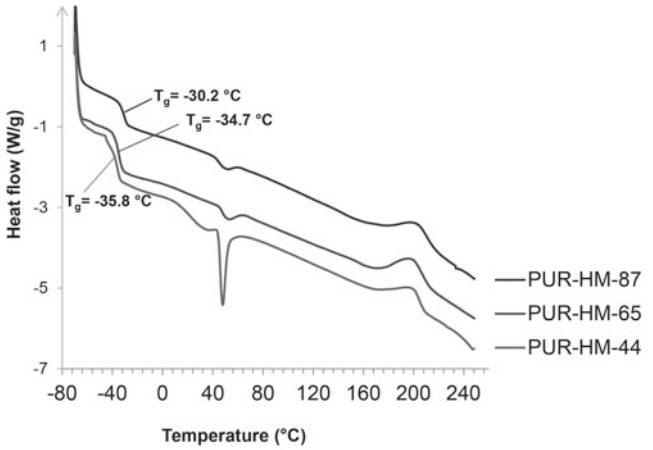


Figure 6. DSC curves of poly(ester-carbonate-urea-urethane)s obtained from IPDI

acetonitrile, DMF). The polyurethane samples based on HDI were insoluble, only an extensive swelling was observed. In contrast to PUR based on IPDI, polyurethanes obtained from HDI are characterized by a regular structure. Higher molecular weight of oligomerols (ca. 3000) also enhances PUR solubility due to the smaller physical crosslinking density.

Thermal analysis of poly(ester-carbonate-urea-urethane)s

Thermal properties of poly(ester-carbonate-urea-urethane)s were characterized by DSC measurements (Table 3). The glass transition temperatures of all samples, independently of carbonate units content, were in the range of –29.2 to –35.8°C. The polyurethanes based on HDI exhibited slightly lower glass transition temperature than those obtained from IPDI. The study showed that IPDI-based polyurethanes (except of PUR-IP-44, Table 4, run 1) were amorphous (Fig. 6). Those obtained using HDI showed a small degree of crystallinity (Fig. 5). The melting point was changing over a very narrow range 41.2–47.5°C. In the case of both diisocyanates used, the exothermic peaks connected to dissociation of hydrogen bonds are visible at ca. 200°C.

Mechanical properties of poly(ester-carbonate-urea-urethane)s

The mechanical properties of the poly(ester-carbonate-urea-urethane)s are presented in Table 4. The hardness of poly(ester-carbonate-urea-urethane)s was measured using the Shore durometer scale A and D. The highest hardness of the investigated samples was observed for polyurethane based on the oligo(tetramethylene suc-

Table 3. Thermal properties of the poly(ester-carbonate-urethane)s

Run	Sample	Diisocyanate	T_m	ΔH_mS	T_g
			°C	J/g	°C
1	PUR-IP-44	IPDI	46.1	2.4	-30.9
2	PUR-HM-44	HMDI	44.6	7.2	-35.8
3	PUR-HM-53	HMDI	47.5	1.3	-35.4
4	PUR-IP-57	IPDI	–	–	-32.3
5	PUR-HM-57	HMDI	43.5	2.3	-35.8
6	PUR-IP-65	IPDI	–	–	-31.2
7	PUR-HM-65	HMDI	46.0	1.0	-34.7
8	PUR-IP-71	IPDI	–	–	-29.2
9	PUR-HM-71	HMDI	41.2	3.0	-32.2
10	PUR-IP-74	IPDI	–	–	-29.2
11	PUR-HM-74	HMDI	44.1	4.1	-33.1
12	PUR-IP-79	IPDI	–	–	-30.5
13	PUR-HM-79	HMDI	44.2	2.0	-34.6
14	PUR-HM-87	HMDI	42.5	2.1	-30.2

a) PUR-IP-44 means poly(succinate-*co*-carbonate-urea-urethane) based on IPDI and oligo(tetramethylene succinate-*co*-carbonate) diol containing 44 mol.% carbonate units.
b) PUR-HM-44 means poly(succinate-*co*-carbonate-urea-urethane) based on HDI and oligo(tetramethylene succinate-*co*-carbonate) diol containing 44 mol.% carbonate units.

cinate-*co*-carbonate) diol characterized by the highest content of crystalline phase and the lowest content of carbonate units (PUR-HM-44). In general, the hardness of the obtained poly(ester-carbonate-urea-urethane)s was in the range of 60–80°Sh A and 20–35°Sh D. For the HDI-based samples the values of hardness were 14–26% higher, than in the case of the IPDI-based analogues.

It was found that the obtained products are characterized by a very good tensile strength (up to 58 MPa) with simultaneous high elongation at break (up to 500%). Similarly to hardness measurements, the higher values of tensile strength (10–50%) were observed for the samples based on HDI. There is no obvious trend in mechanical properties as a function of carbonate units content. All samples after stretching and releasing the stretching force returned to their initial shape immediately, which indicates that those samples have elastomeric properties.

Biodegradation of poly(ester-carbonate-urea-urethane)s

For biodegradation tests two lipases: *Pseudomonas cepacia* and *Pseudomonas* sp. were selected due to their good activity in poly(ester-urethane) degradation[18, 19]. The rate of biodegradation was measured as a weight loss in time. The preliminary results indicated that only the samples of PUR-IP with the content of carbonate units lower than 65 mol% exhibited the weight loss higher than 2% after 7 months. The highest biodegradation rates were observed in the presence of *Pseudomonas* sp. enzyme: 20.9% PUR-IP-41, 14.8% PUR-IP-57 and 6.0% PUR-IP-65. The rates of poly(ester-carbonate-urea-urethane)s biodegradation in the presence of *Pseudomonas cepacia* lipase enzyme and hydrolytic degradation in buffer (pH = 7.280) were similar (Figs. 7–9). What is more, samples with the carbonate units in the range of 41–65 mol% were characterized with no crystalline phase, that additionally influenced the biodegradation process.

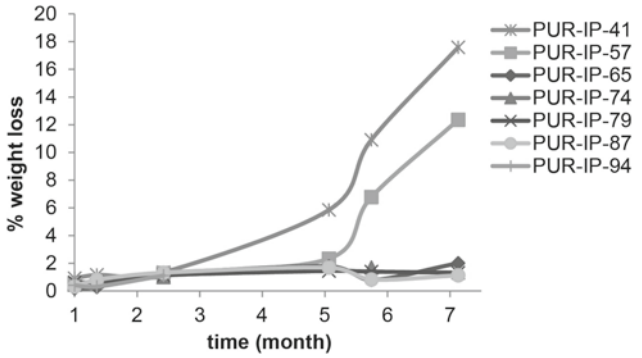


Figure 7. Weight loss against time of the hydrolysis of poly(ester-carbonate-urea-urethane)s with a different amount of carbonate units in phosphate buffer solution (pH = 7.280)

Table 4. Mechanical properties of poly(ester-carbonate-urethane)s

Run	Sample	Diisocyanate	Tensile strength	Elongation at break	Hardness	Hardness
			MPa	%	°Sh A	°Sh D
1	PUR-IP-44	IPDI	29.0 ± 0.4	460 ± 15	76 ± 2	33 ± 2
2	PUR-HM-44	HMDI	43.2 ± 5.0	630 ± 14	96 ± 2	37 ± 6
3	PUR-HM-53	HMDI	57.6 ± 8.3	500 ± 76	74 ± 2	24 ± 1
4	PUR-HM-57	HMDI	34.3 ± 2.2	545 ± 20	74 ± 3	27 ± 1
5	PUR-IP-65	IPDI	18.4 ± 0.3	570 ± 8	67 ± 1	22 ± 1
6	PUR-HM-65	HMDI	38.4 ± 3.5	520 ± 13	77 ± 2	31 ± 2
7	PUR-IP-71	IPDI	13.3 ± 1.1	560 ± 2	65 ± 1	21 ± 1
8	PUR-HM-71	HMDI	24.1 ± 1.5	515 ± 10	74 ± 2	34 ± 2
9	PUR-IP-74	IPDI	24.9 ± 3.9	490 ± 25	67 ± 1	23 ± 1
10	PUR-HM-74	HMDI	27.0 ± 6.2	440 ± 6	78 ± 2	34 ± 1
11	PUR-HM-79	HMDI	20.8 ± 3.3	530 ± 3	71 ± 2	33 ± 2
12	PUR-HM-87	HMDI	42.4 ± 7.3	430 ± 7	76 ± 1	28 ± 1

a) PUR-IP-44 means poly(succinate-*co*-carbonate-urea-urethane) based on IPDI and oligo(tetramethylene succinate-*co*-carbonate) diol containing 44 mol.% carbonate units.
b) PUR-HM-44 means poly(succinate-*co*-carbonate-urea-urethane) based on HDI and oligo(tetramethylene succinate-*co*-carbonate) diol containing 44 mol.% carbonate units.

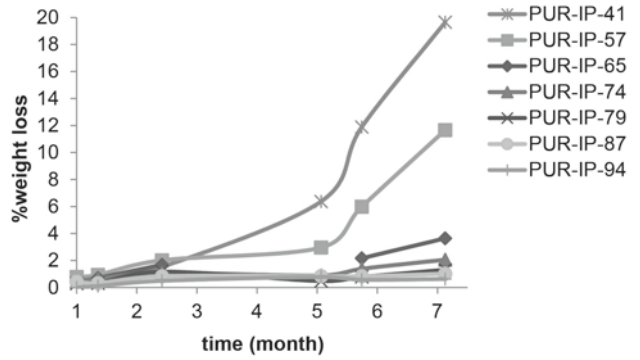


Figure 8. Weight loss against the time of the hydrolysis of poly(ester-carbonate-urea-urethane)s with different amount of carbonate units in phosphate buffer solution (pH = 7.283) in the presence of *Pseudomonas cepacia* enzyme

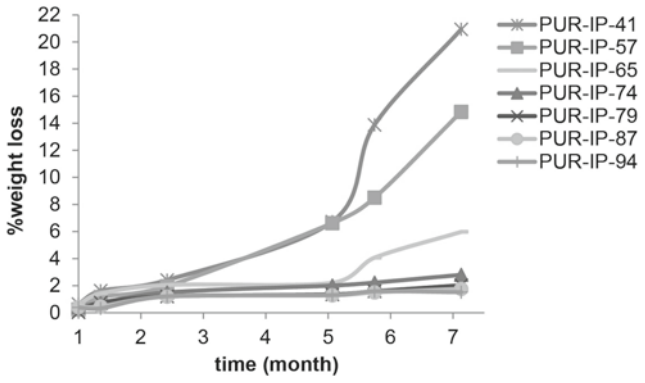


Figure 9. Weight loss against time of the hydrolysis of poly(ester-carbonate-urea-urethane)s with a different amount of carbonate units in phosphate buffer solution (pH = 7.283) in the presence of *Pseudomonas* sp. enzyme

CONCLUSIONS

A new method of the synthesis of aliphatic oligo(ester--carbonate) diols was elaborated. The use of tetramethylene bis(methyl carbonate) as a source of carbonate linkages enables the introduction of an appropriate amount of carbonate units into oligomerols of planned molecular weight. It was found that oligo(tetramethylene succinate-*co*-carbonate) diols containing 57–74 mol% of carbonate units are amorphous. Poly(ester-carbonate--urea-urethane)s based on oligo(ester-carbonate) diols and aliphatic HDI diisocyanate are characterized by higher hardness as well as tensile strength than those obtained from cycloaliphatic IPDI. In contrast to PUR-HM, PURs based on IPDI, due to weaker hydrogen bonding of hard segments, are soluble at room temperature in typical solvents such as $CHCl_3$, CH_3CN and DMSO. The preliminary results of the biodegradation test indicate that poly(ester-carbonate-urea-urethane)s containing 40 to 65 mol% of carbonate units in amorphous soft segments undergo hydrolytic as well as enzymatic degradation – up to 20% weight loss after 7 months.

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