Polyurethane elastomers based on carbonic and tartaric acid derivatives as renewable resources*)

Gabriel Rokicki1), **), **Magdalena Mazurek**1), **Karolina Tomczyk**1)

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Abstract: In the present study, three methods of introduction of the tartaric acid derivative into poly(carbonate-urethane)s chemical structure are presented and discussed. Tartaric acid derivative containing two free and two protected OH groups was introduced according to polycondensation, ring opening polymerization (in oligocarbonate synthesis step) and polyaddition (in prepolymer synthesis step as a chain extender) reactions. The prepared poly(carbonate-urethane)s were characterized by NMR and FT-IR spectroscopies, DSC and TGA thermal analyses, and mechanical properties measurements. The influence of the introduced tartaric acid derivative on properties of oligocarbonates and polyurethanes was investigated.

Keywords: poly(carbonate-urethane), oligocarbonate diol, tartaric acid, (*4S,5S*)-4,5-bis(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane.

Elastomery poliuretanowe otrzymywane z surowców odnawialnych — pochodnych kwasu węglowego i winowego

Streszczenie: Opisano trzy sposoby wbudowania do struktury poli(węglano-uretanów) pochodnej kwasu winowego, zawierającej dwie wolne i dwie zablokowane grupy OH, z wykorzystaniem polikondensacji, polimeryzacji z otwarciem pierścienia (na etapie syntezy oligowęglanodioli) i poliaddycji stopniowej (na etapie syntezy prepolimeru jako przedłużacza łańcucha). Otrzymane poli(węglano-uretany) scharakteryzowano metodami spektroskopii NMR i FT-IR, analizy termicznej DSC i TGA oraz za pomocą pomiarów wytrzymałości mechanicznej. Oceniono wpływ zawartości pochodnej kwasu winowego na właściwości oligowęglanów i poliuretanów.

Słowa kluczowe: poli(węglano-uretany), oligowęglanodiole, kwas winowy, (*4S,5S*)-4,5-bis(hydroksymetylo)-2,2-dimetylo-1,3-dioksolan.

In everyday life elastomeric, segmented polyurethanes (PUR) have many applications mainly because of their excellent mechanical and chemical properties [1]. Due to these characteristics, their utilization has been rapidly extended to the field of biomedical applications such as soft tissue interfacing materials, arteriovenous access grafts, catheters, prosthetic valve leaflets, and compliant vascular grafts [2].

Experimental findings indicate that poly(ester-urethane)s rapidly undergo hydrolytic degradation [3, 4], whereas poly(ether-urethane)s are hydrolytically stable but susceptible to oxidative degradation in various forms, including metal ion oxidation, autooxidation, and environmental stress cracking [5].

Recently, more attention has been paid to poly(carbonate-urethane)s. This type of PURs exhibit higher hydrolytic resistance than that of poly(ester-urethane)s and higher oxidative resistance in comparison to poly(ether-urethane)s. Moreover, these polyurethanes exhibit outstanding mechanical properties. In contrast to poly(ester-urethane)s, inhibited hydrolysis of oligocarbonate segments does not lead to pH decrease, due to the formation of alcohol derivatives and CO_2 instead of carboxylic acid as the degradation products. Taking the above into account, several studies have been attempted to make oligocarbonate segment more susceptible to hydrolytic biodegradation.

One of the approaches based on using oligo(ester-carbonate)s as a oligomerols for polyurethane synthesis. Depending on aliphatic ester units content the hydrolysis rate can be precisely tuned. Such oligo(ester-carbonate)s are prepared according to copolymerization of six-membered carbonates with cyclic esters such as lactide [6—8], glycolide [9, 10], ε-caprolactone [11] or in polycondensation mode using diphenyl carbonate, diethyl- or dimethyl carbonate as a source of carbonate linkages with aliphatic dicarboxylic acids and diols [12, 13].

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[1] Warsaw University of Technology, Faculty of Chemistry, Department of Polymer Chemistry and Technology, ul. Noakowskiego 3, 00-664 Warsaw, Poland.

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[**] Author for correspondence; e-mail: gabro@ch.pw.edu.pl

There are only a few reports concerning poly(ester-carbonate-urethane)s. Wagner and coworkers synthesized PUR based on poly(ε-caprolactone), poly(hexamethylene carbonate) and 1,4-butylene diisocyanate [14]. Sobczak *et al.* used ε-caprolactone in the copolymerization with trimethylene carbonate and neopentyl carbonate. The resultant oligomerol was used as a soft segment in the reaction with MDI (methylene diphenyl diisocyanate), 1,4-butanediol and putrescine as a chain extender [15].

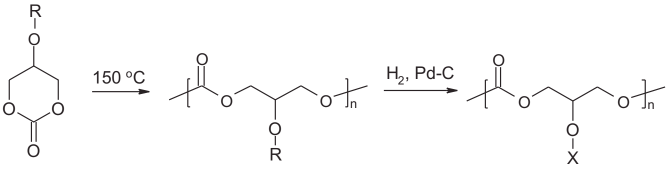
Very recently, Mazurek *et al.* obtained poly(ester-carbonate-urethane)s from oligo(tetramethylene succinate-*co*-carbonate) diols using dimethyl succinate, 1,4-butanediol and tetramethylene bis(methyl carbonate), aliphatic diisocyanates (IPDI) as starting materials and water as a chain extender [16] or aliphatic-aromatic ester-carbonate oligomerols based on poly(ethylene terephthalate) (PET) wastes and dimethyl carbonate as a source of carbonate units [17]. These polyurethanes exhibited much higher biodegradation rate in comparison to that of poly(carbonate-urethane). Hong *et al.* used a blended soft segment of poly(ε-caprolactone) (PCL) and poly(1,6-hexamethylene carbonate) (PHC), a 1,4-diisocyanatobutane hard segment and chain extension with putrescine for obtaining poly(ester-carbonate-urethane)ureas [14].

In other approach oligocarbonate with pendent, blocked hydrophilic groups can be used as oligomerols in the synthesis of polyurethanes with hydrophilic properties.

Zhuo *et al.* synthesized polycarbonate with pendent hydroxyl groups. Water-soluble polycarbonate with primary OH groups was prepared from 2-(2-benzyloxyethoxy)trimethylene carbonate (Scheme A a) [18, 19].

A similar method was reported by the Zhuo group for obtaining polycarbonate with pendent, secondary hydroxy groups through ROP of 5-benzyloxy-trimethylene carbonate (Scheme A b) [20—23].

Hoecker and coworkers obtained polycarbonate with pendent hydroxymethyl groups by polymerization of 5-ethyl-5-hydroxymethyl-1,3-dioxan-2-one with blocked OH group [24].



R = CH_2Ph and X = H (a) or R = $CH_2CH_2OCH_2Ph$ and X = CH_2CH_2OH (b)

Scheme A

Xie *et al.* used the pentaerithritol carbonate-derivative for synthesis of polycarbonate with two pendent, hydroxymethyl groups in geminal position (Scheme B) [25]. OH groups were protected by six-membered cyclic acetals.

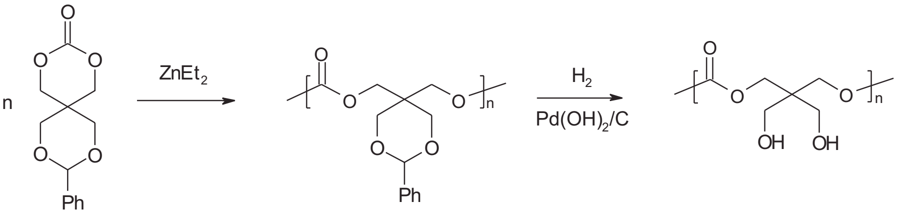
Bisht and co-workers [26—28] and Storey and co-workers [29] prepared polycarbonate with pendent, blocked carboxylic acid groups (Scheme C).

Zhuo and co-workers used dihydroxyacetone as starting material for obtaining polycarbonates with hydrophilic groups in the main backbone [30, 31]. Putnam *et al.* used also dihydroxyacetone for obtaining poly(lactide-*co*-dihydroxyacetone) copolymers [32]. A dimethoxy acetal protecting group was used to stabilize the dihydroxyacetone carbonate and was removed using iodine and acetone at reflux.

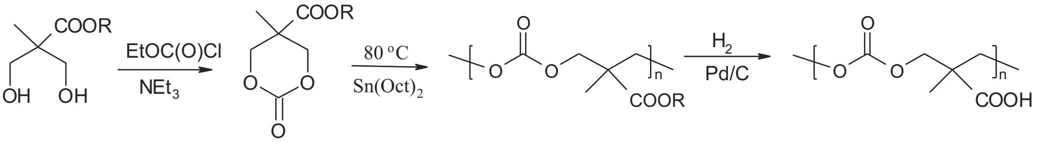
Few examples of using tartaric acid and its derivatives in order to increase the hydrophilic properties of polymers were reported. This natural, cheap and easily available starting material [33, 34] was built-in into main backbones of polyamides [35—37], poly(ester-amide)s [38, 39], polyesters [40—42], and polycarbonates [43, 44]. Ahlers and co-workers obtained polyester based exclusively on tartaric acid and its acid chlorides (Scheme D, synthesis carried out under phase-transfer catalysis) [45].

Biodegradation carried out *in vivo* indicated that polymers based on tartaric acid or its derivatives are biocompatible. Schliecker *et al.* revealed that such polymer degraded in 90 % after 30 days in pH 7.4 phosphate buffer solution at 37 °C [46].

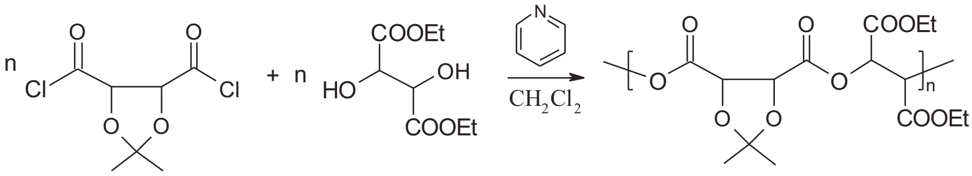
Bisht and co-workers synthesized hydrophilic polycarbonate by polymerization or copolymerization of



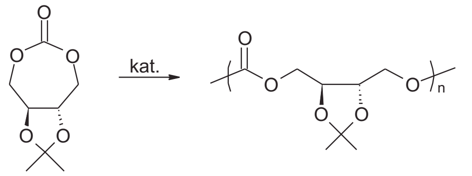
Scheme B



Scheme C



Scheme D



Scheme E

seven-membered cyclic tartaric acid derivative (Scheme E) [47, 48].

Polycarbonates with pendent functional groups, based on 1,4:3,6-dianhydrohexitols and L-tartaric acid derivatives were synthesized also by Yokoe *et al*. [49].

In this article the new methods of obtaining poly(carbonate-urethane)s based on carbonate oligomerols containing the build-in tartaric acid derivative [(4*S*,5*S*)-4,5-bis(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane — (**3**)] are described and discussed. The tartaric acid derivative with protected hydroxyl groups in 2,3 positions was introduced into polyurethane chemical structure according to polycondensation mode as an oligocarbonate diol component or as a chain extender in urethane prepolymer formation.

EXPERIMENTAL PART

Materials

— 1,3-propanediol (98 %), 1,4-butanediol (99 %), hexamethylene diisocyanate (HDI) (98 %), tetramethylene diisocyanate (TMDI) (97 %), isophorone diisocyanate (IPDI) (98 %), titanium(IV) butoxide (97 %) (Aldrich),

— anhydrous K_2CO_3, anhydrous $MgSO_4$, methanol, ethyl acetate, toluen, 1,4-dioxane (POCh),

— dimethyl carbonate (DMC) (99 %), 2,2-dimethoxypropane (98 %), lithium aluminum hydride (95 %), *p*-toluenesulfonic acid (≥98.5 %) (Sigma-Aldrich),

— L-tartaric acid (Laboratory of Technological Processes (LPT) Faculty of Chemistry, Warsaw University of Technology) were used as received.

— Tetrahydrofuran and diethyl ether (POCH) were purified in a conventional manner.

Synthesis of oligocarbonate diols based on dimethyl carbonate and α,ω-diols

Oligocarbonate diols were synthesized following the two-step condensation procedure already published by us [50, 51]. In the first step alkylene bis(methylcarbonate) (BMC) was obtained in the reaction of dimethyl carbonate (DMC) (used in molar excess) with α,ω-diol in the presence of a transesterification catalyst. The resultant tetramethylene bis(methylcarbonate) was a white solid, whereas trimethylene bis(methylcarbonate) were colorless liquids. Then, the BMC was used in the polytransesterification process with appropriate α,ω-diol to obtain oligocarbonate diol.

Synthesis of oligo(trimethylene carbonate) diol

In a 10 cm^3 round-bottomed flask equipped with a magnetic stirrer and thermometer and nitrogen inlet 2.59 g (0.03 mol) of trimethylene carbonate and 0.17 g (2.24 mmol) of 1,3-propanediol were placed. The reaction was carried out at 110 °C for 24 h. Obtained products were in a form of viscous, colorless liquid. Reactions were repeated with various molar ratios of reactants.

^1H NMR (400 MHz, $CDCl_3$); δ (ppm) = 4.25 (t, $C\underline{H}_2CH_2CH_2OH$), 4.19 [t, $CH_2OC(O)O$], 3.69 (q, $C\underline{H}_2OH$), 2.01 [p, $C\underline{H}_2CH_2OC(O)O$], 1.87 (dt, $C\underline{H}_2CH_2OH$). ^{13}C NMR (400 MHz, DMSO-d_6); δ (ppm) = 154.5 (C=O), 64.3 (CH_2O), 27.6 ($\underline{C}H_2CH_2O$). FT-IR (KBr); ν (cm^{-1}) = 3492, 2945—2864, 1738, 1251—1020, 790.

Preparation of tartaric acid derivatives

Synthesis of (2*R*,3*R*)-dimethyl tartrate (1)

In a 250 cm^3 round-bottomed flask equipped with a magnetic stirrer, Soxhlet apparatus filled with molecular sieves type 3A and a reflux condenser, 50.00 g (0.33 mol) of L-tartaric acid, 55 cm^3 (1.36 mol) of methanol and 0.63 g (3.30 mmol) of *p*-toluenesulfonic acid were placed. The synthesis was carried out at the boiling point of the reaction mixture. The reaction was monitored by thin layer chromatography (TLC). Excess of methanol was distilled off under reduced pressure. Then the reaction mixture was dissolved in ethyl acetate, washed three times with 5 % K_2CO_3 water solution, dried over $MgSO_4$, and crystallized. The obtained product was recrystallized from ethyl acetate to give 34.4 g of (2*R*,3*R*)-dimethyl tartrate **(1)** (yield 58 %) of T_m = 58—60 °C.

^1H NMR (400 MHz, DMSO-d_6); δ (ppm) = 5.52 (d, 2H, OH, *J* = 7.2 Hz), 4.40 (d, 2H, CH, *J* = 6.1 Hz), 3.65 (s, 1H, CH_3). FT-IR (KBr); ν (cm^{-1}) = 3410 (O-H), 2981—2878 (C-H), 1747 (C=O), 1281—1235 (C-O), 1133—1091 (C-O).

Synthesis of (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylic acid dimethyl ester (2) [49]

In a 250 cm^3 three-neck round-bottomed flask equipped with magnetic stirrer and thermometer 45.00 g (0.25 mol) of dimethyl tartrate (**1**), 93 cm^3 (0.76 mol) 2,2-dimethoxypropane (DMP), 1.29 g (7.50 mmol) *p*-toluenesulfonic acid (TSA) and 50 cm^3 of toluene were placed. The reaction was carried out at 40—70 °C for 4 hours. Change of the reaction mixture color to dark red was observed. The reaction was monitored by TLC. After cooling the reaction mixture to room temperature, 0.5 g of K_2CO_3 was added and stirred for 10 minutes during which color change from dark red to yellow was observed. Then the precipitate was filtered off. Excess of the substrate and solvent were distilled off under reduced pressure, and the residue was subjected to vacuum distillation. 38.7 g of a yellow, oily liquid (yield 71 %) fraction with boiling point of 116 °C (*p* = 0.8 kPa) was collected.

^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 4.74 (s, 2H, CH), 3.76 (s, 6H, OCH_3), 1.42 (s, 6H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$); δ (ppm) = 169.8 (C=O), 113.58 (C), 76.7 (CH), 52.5 (OCH_3), 26.1 (CH_3). FT-IR (KBr); ν (cm^{-1}) = 2995—2958 (C-H), 1762 (C=O), 1257—1213 (C-O).

Synthesis of (4*S*,5*S*)-4,5-bis(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane (3) [49]

In a 250 cm^3 three-neck round-bottomed flask equipped with magnetic stirrer, thermometer, reflux condenser, dropping funnel and nitrogen supply system 4.18 g (0.11 mol) of lithium aluminum hydride and 50 cm^3 of anhydrous diethyl ether were placed. Within an hour, 12.0 g (0.055 mol) of dimethyl ester of (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylic acid (**2**) dissolved in 50 cm^3 of diethyl ether was added dropwise. After 12 hours methanol was added portionwise to decompose the excess lithium aluminum hydride. Reaction mixture was filtered under reduced pressure. Precipitate was washed with 20 % sodium hydroxide solution and poured into a separatory funnel. The product was extracted three times with 50 cm^3 of ethyl acetate and dried over magnesium sulfate. The solvent was distilled off under reduced pressure, and the residue was subjected to vacuum distillation. 6.53 g of a light yellow, oily liquid fraction (yield 73 %) with a boiling point at 113—114 °C (*p* = 0.2 kPa) were obtained.

^{1}H NMR (400 MHz, DMSO-d_6); δ (ppm) = 4.90—4.77 (bs, 2H, OH), 3.75—3.72 (m, 2H, CH), 3.54—3.42 (bs, 4H, CH_2), 1.28 (s, 6H, CH_3). ^{13}C NMR (400 MHz, DMSO-d_6); δ (ppm) = 109.1 (C), 78.3 (CH), 62.1 (CH_2) 26.7 (CH_3). FT-IR (KBr); ν (cm^{-1}) = 3435 (O-H), 2983—2870 (C-H), 1068 (C-O).

Synthesis of 4,5-bis(methoxycarbonyloxymethyl)-2,2-dimethyl-1,3-dioxolane (4)

Synthesis was performed in a similar manner as in case of alkylene bis(methylcarbonate). 3.97 g (0.01 mol) of tartaric acid derivative (**3**) was reacted with 12.85 g (0.14 mol) of DMC in the presence of 0.02 g (0.10 mmol) of K_2CO_3. 6.60 g (yield 95 %) of the product was obtained in form of yellow, viscous liquid.

^{1}H NMR (400 MHz, DMSO-d_6); δ (ppm) = 4.24 (dddd, 4H, CH_2, J_1 = 1.5 Hz, J_2 = 2.9 Hz, J_3 = 5.1 Hz, J_4 = 11.5 Hz), 4.05 (dt, 2H, CH, J_1 = 1.8 Hz, J_2 = 4.1 Hz), 3.74 (s, 6H, $CH_3OC(O)O$), 1.36 (s, 6H, $C(CH_3)_2$). FT-IR (KBr); ν (cm^{-1}) = 2969—2875 (C-H), 1744 (C=O), 1263—1081 (C-O).

Synthesis of carbonate oligomerols containing tartaric acid derivative (3)

Synthesis of oligocarbonate diols in the reaction of tartaric acid derivative (4) with α,ω-diols

Synthesis was carried out in a similar manner as in case of unmodified oligocarbonate diol, but instead of alkylene bis(methylcarbonate) 4.49 g (0.016 mol) of bis(methylcarbonate) derivative of tartaric acid (**4**) was used in the reaction with 1.47 g (0.020 mol) of 1,4-butanediol. Product was obtained in form of yellow, viscous liquid. Reactions were carried out with various α,ω-diols and molar ratios of the reactants.

BC_T40_2140: ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 4.37—4.20 (m, $C\underline{H}_2CH$), 4.19—4.12 (m, $CH_2OC(O)O$), 4.11—4.07 (m, CH), 3.70—3.65 (m, $C\underline{H}_2OH$), 1.79—1.74 (m, $C\underline{H}_2CH_2OC(O)O$), 1.41 (s, CH_3). FT-IR (KBr); ν (cm^{-1}) = 3513, 2987—2867, 1747, 1257—1093, 790.

Synthesis of oligocarbonate diols from trimethylene carbonate and tartaric acid derivative (3)

Synthesis was carried out in a similar manner as in case of unmodified oligo(trimethylene carbonate) diol. 2.12 g (0.02 mol) of trimethylene carbonate and 0.29 g (1.81 mmol) of tartaric acid derivative (**3**) were used in the reaction. Product was obtained in form of colorless, viscous liquid. Other synthesis were carried out with various molar ratios of the reactants.

PC_T11_2070: ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 4.37—4.31 (m, $C\underline{H}_2CH$), 4.30 (t, $C\underline{H}_2CH_2CH_2OH$, *J* = 6.1 Hz), 4.23 (t, $CH_2OC(O)O$, *J* = 6.3 Hz), 4.11—4.07 (m, CH), 3.73 (dd, $C\underline{H}_2OH$, J_1 = 5.9 Hz, J_2 = 11.7 Hz), 2.05 (p, $C\underline{H}_2CH_2OC(O)O$, *J* = 6.2 Hz), 1.95—1.88 (m, $C\underline{H}_2CH_2OH$). FT-IR (KBr); ν (cm^{-1}) = 3549, 2972—2910, 1744, 1242—1033, 791.

Preparation of poly(carbonate-urethane)s

Poly(carbonate-urethane)s were obtained according to the procedure already reported by us [51]. 3-molar excess of diisocyanate to oligomerol was used. Reaction was carried out without usage of any catalyst or solvent, under nitrogen atmosphere at 80 °C until a disappearance of an absorption band characteristic for OH groups (3500 cm^{-1}) in the FT-IR spectrum of the product was observed. Then, the relatively high viscosity urethane prepolymers were deaerated under reduced pressure. The process of chain extending of urethane prepolymer was performed on open glass forms in a climatic chamber under controlled conditions of humidity and temperature.

Methods of testing

— ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR 400 MHz spectrometer using tetramethylsilane as an internal standard, and $CDCl_3$ as a solvent and analyzed with MestReNova v.6.2.0-7238 (Mestrelab Research S.L.) software.

— FT-IR spectra of oligocarbonate diols were recorded on a Biorad FT-IR Spectrometer FTS 165 operating in the spectral range of 4000—400 cm^{-1} with 2 cm^{-1} resolution and using 32 counts. Samples were prepared in the form of thin layers of substances applied at KBr pellet.

— Differential scanning calorimetry (DSC) studies were carried out using a TA Instruments DSC Q200. Aluminum pans containing 10—15 mg of sample were heated over a temperature range from -100 to 100 °C with heating rate 5 °C/min, then cooling backward to -100 °C with cooling rate 10 °C/min and heating again with rate 20 °C/min.

— Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449C derivatograph. The analysis was conducted with a heating rate of 5 °C/min from room temperature to 800 °C, in a constant flow of gases: argon (shielding gas) 10 cm^3/min and synthetic air (N_2:O_2 — 3:1) 40 cm^3/min.

— Mechanical properties of polyurethanes were determined using the Instron 5566 Universal Testing Machine. Head speed — 5 % length/min. Measurements were conducted with standard samples (5 for each polymer) (ISO 527-2/1BA) cut from films with thickness of 1 mm.

RESULTS AND DISCUSSION

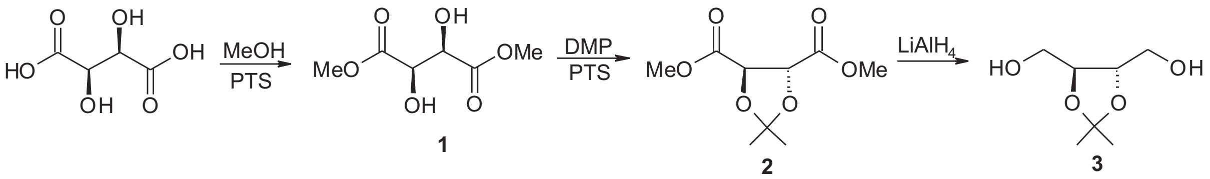
Synthesis of oligocarbonate diols

In the presented work, obtained oligocarbonate diols were used for preparation of polyurethanes according to a prepolymer method synthesis using aliphatic isocyanates (isophorone, hexamethylene or tetramethylene diisocyanate) and water vapor as a chain extender. In order to increase the hydrophilic properties of oligocarbonate diols, tartaric acid derivative (**3**) was introduced into their chemical structure. Prior to use of tartaric acid for modification of hydrophilic properties of oligocarbonate its hydroxyl groups should be protected by a cyclic acetal and ester groups reduced to hydroxy methyl ones. Tartaric acid derivative — (4*S*,5*S*)-4,5-bis(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane (**3**) was obtained in three steps described in detail in experimental section (Scheme F). At first tartaric acid methyl ester was treated with 2,2-dimethoxypropane (DMP) under acidic conditions, followed by $LiAlH_4$ reduction of the resulting (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylic acid dimethyl ester (**2**) to afford (**3**).

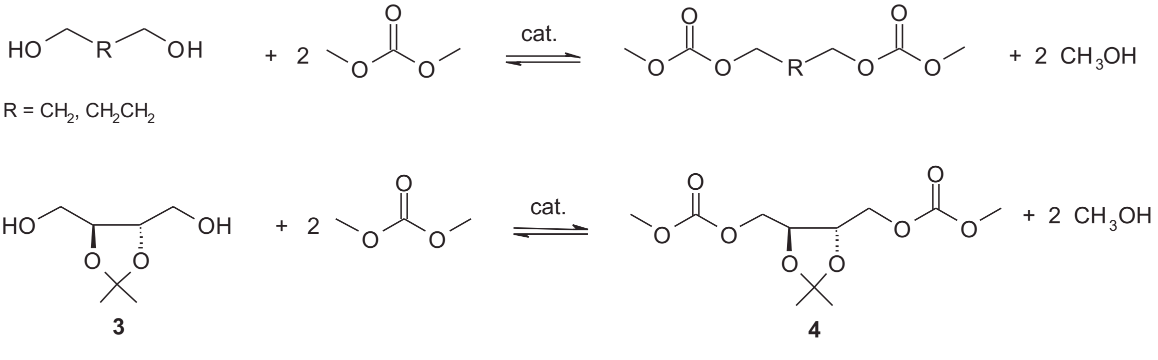
Synthesis of oligocarbonate diols using dimethyl carbonate (DMC) as a source of carbonate linkages

In the first step, as a result of the reaction between diol with excess of DMC, the semiproduct — alkylene bis(methylcarbonate)s (BMC) — were obtained (Scheme G). Resultant tetramethylene bis(methylcarbonate) was a white solid, whereas trimethylene bis(methylcarbonate) and bis(methylcarbonate) derivative of tartaric acid (**4**) were liquids of high viscosity.

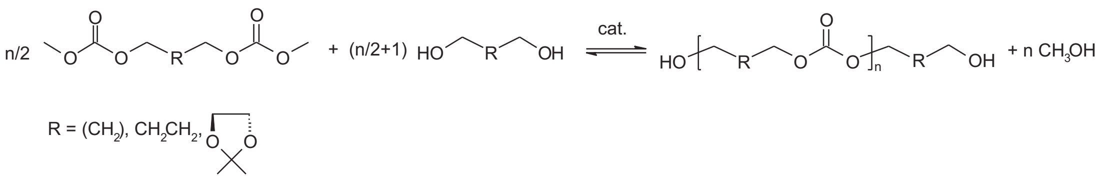
In the second step in the reaction of BMC and appropriate diol, oligocarbonate diols and oligocarbonate diols



Scheme F



Scheme G



Scheme H

T a b l e 1. Characteristics of oligocarbonate diols obtained by polycondensation of alkylene bis(methylcarbonate)

Sample	Diol	Diol / BMC	M_n d), g/mol	Content of (**3**), mol %	T_g, °C	T_m, °C
PC_1530 a)	1,3-propanediol	1.05/1	1530	-	-30.4	e)
BC_1680 b)	1,4-butanediol	1.05/1	1680	-	-43.4	51.2
BC_T40_2140 c)	1,4-butanediol	1.02/1	2140	40	-14.2	e)

a) **PC_1530** — oligo(trimethylene carbonate) diol of $M_n = 1530$ g/mol.

b) **BC_1680** — oligo(tetramethylene carbonate) diol of $M_n = 1680$ g/mol.

c) **BC_T40_2140** — oligo(tetramethylene carbonate) diol modified with 40 mol % of tartaric acid derivative (**4**) of $M_n = 2140$ g/mol.

d) Molar mass estimated from ^{1}H NMR.

e) Melting point was not observed in the thermogram.

modified with tartaric acid derivative (**4**) were obtained, respectively. (Scheme H, Table 1).

Synthesis of oligocarbonate diols based on trimethylene carbonate (TMC)

For the synthesis of oligocarbonate diols by ring-opening polymerization trimethylene carbonate was used. As a starter-initiator 1,3-propanediol, 1,4-butanediol and tartaric acid derivative (**3**) were used (Scheme I).

Depending on the molar ratio of trimethylene carbonate to the starter-initiator number average molar mass were in the range of 1160 to 3710 g/mol. Due to mild reaction conditions (110 °C) no loss of tartaric acid derivative (**3**) in oligomerol was observed (Table 2).

Molecular structures of the obtained oligocarbonate diols were confirmed with NMR spectroscopy. The exemplary ^{1}H NMR spectrum of the oligocarbonate diol containing tartaric acid derivative (**3**) (**PC_T11_2070**) is shown in Fig. 1. Chemical shift of the triplet at 4.23 ppm corresponding to the protons of the methylene group in the vicinity to the carbonate group as well as the signal from the built-in tartaric acid derivative (**3**) at 4.37— 4.31 ppm corresponding to the protons of the methylene group in the vicinity of the carbonate group, a multiplet at 4.11—4.07 ppm derived from methine protons and a singlet at 1.42 ppm derived from the protons of the methyl group, as well as the signal from the protons of the terminal group at a chemical shift of 4.09 ppm can be observed.

Thermal properties of oligocarbonate diols

Thermal analysis of oligocarbonate diols was performed using DSC technique (Table 1, Table 2). Oligo-

T a b l e 2. Characteristics of oligocarbonate diols obtained by ring-opening polymerization of trimethylene carbonate with different starters

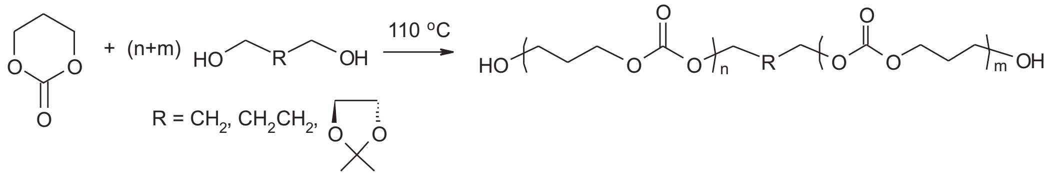
Sample	Starter-initiator	TMC / starter	M_n d), g/mol	Content of (**3**), mol %	T_g, °C
PC_1160	1,3-propanediol	11.5/1	1160	-	-33.8
PBC_1210	1,4-butanediol	11.0/1	1210	-	-36.9
PC_T11_2070	tartaric acid derivative (**3**)	11.5/1	2070	11	-23.3
PC_T4_3710		32.5/1	3710	4	-21.1

a) **PC_1160** — oligo(tetramethylene carbonate) diol of $M_n = 1160$ g/mol.

b) **PBC_1210** — oligo(trimethylene/tetramethylene carbonate) diol of $M_n = 1210$ g/mol with 9 mol % of tetramethylene carbonate units.

c) **PC_T11_2070** — oligo(trimethylene carbonate) diol modified with 11 mol % of tartaric acid derivative (**3**) of $M_n = 2070$ g/mol.

d) Molar mass estimated from ^{1}H NMR.



Scheme I

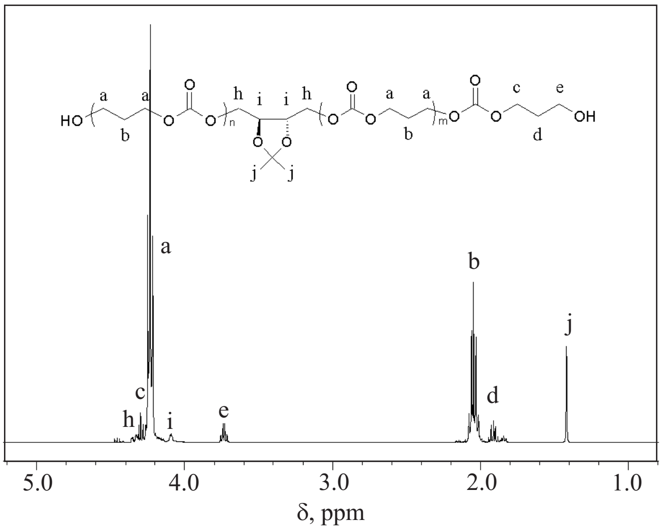


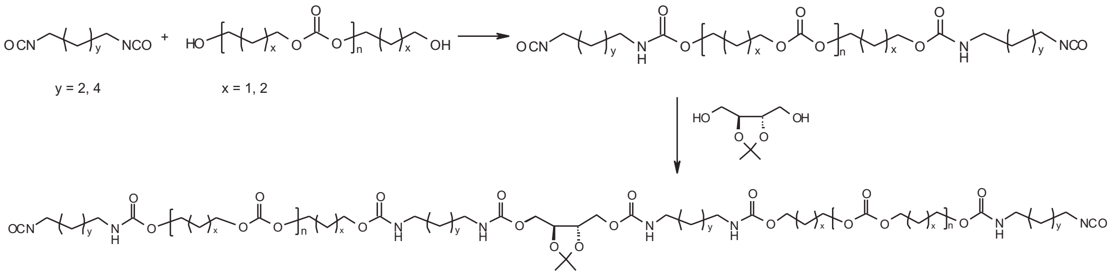
Fig. 1. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of oligocarbonate diol based on TMC and tartaric acid derivative (3) (PC_T11_2070)

mers obtained from 1,3-propanediol were characterized by a glass transition temperature (T_g) around -30 °C, depending on molar mass. When 9 mol % of tetramethylene carbonate units was additionally incorporated (**PBC_1210**) T_g decreased to -36.9 °C, whereas unmodified oligo(tetramethylene carbonate) diol (**BC_1680**) shown T_g = -43.4 °C. When tartaric acid derivative (**3**) was introduced to oligo(trimethylene carbonate), T_g increased to -23.3 °C (**PC_T11_2070**) and to -21.1 °C (**PC_T4_3710**). The highest glass transition temperature of -14.2 °C was observed when 40 mol % tartaric acid derivative (**4**) was incorporated into oligo(tetramethylene carbonate) (**BC_T40_2140**). Only in case of **BC_1680** melting of soft segment crystallites was observed at T_m around 50 °C.

Synthesis of poly(carbonate-urethane)s

To obtain poly(carbonate-urethane)s two-step prepolymer method was applied. Usually, polymers obtained in this manner are characterized by better formed segmented structure [52]. The reaction was carried out at 80 °C under an inert gas atmosphere without any catalyst and solvent [53]. Performing the synthesis at temperature lower than 90 °C prevents reactions leading to the formation of allophanate bond and dimerization or trimerization of isocyanate. Used threefold molar excess of diisocyanate in relation to oligomerol prevents the chain extension and increases the content of hard segments [54]. Tartaric acid derivative (**3**) was incorporated into polyurethane chemical structure also as a chain extender in the step of urethane prepolymer preparation (Scheme K).

Prepolymers were poured into open glass forms, deaerated under reduced pressure and then cured in climatic chamber under optimized conditions of temperature and humidity [51]. As a result of hydrolysis of isocyanate groups amino groups were formed and on the further step undergo reaction with next isocyanate group leading to chain extension. The rate of reaction of the amino group with isocyanate is much higher than the rate of hydrolysis of an isocyanate group, thus not all the isocyanate groups are hydrolyzed (Scheme L). After 7 days unexpanded, transparent and colorless polyurethane films were obtained.



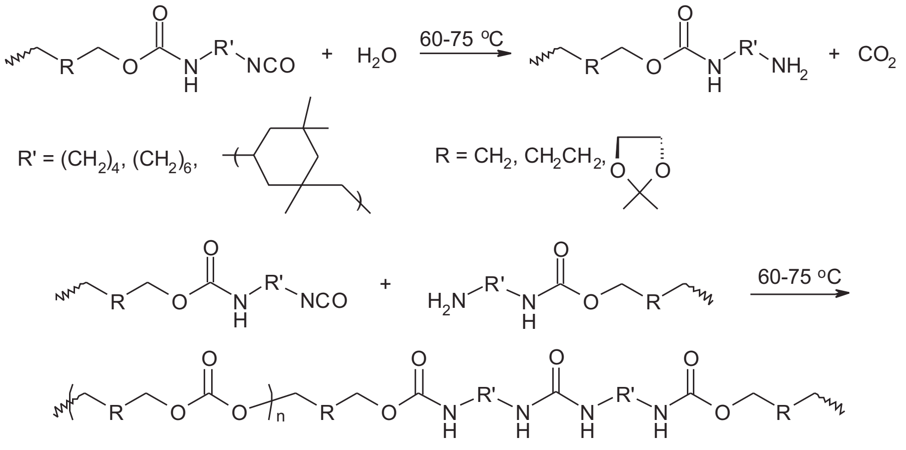
Scheme K

Poly(carbonate-urethane)s modified with tartaric acid derivative obtained from hexamethylene and tetramethylene diisocyanate, in contrast to those obtained from isophorone isocyanate were soluble in DMSO, enabling the analysis of the structure by NMR spectroscopy. Also based on ^{1}H NMR spectra amount of built-in derivative was determined — from 7 to 16 mol % of tartaric acid derivative (**3**) was incorporated. Exemplary spectrum of poly(carbonate-urethane) based on oligocarbonate diol obtained in ROP reaction of TMC with tartaric acid derivative (**3**) and tetramethylene diisocyanate (**PUR-PC_1530-T8-TMDI)** is showed in Fig. 2.

Thermal properties of poly(carbonate-urethane)s

Thermal analysis of obtained polyurethanes was performed using DSC and TGA. Polyurethanes containing tartaric derivative were compared with those without modifier.

Polyurethanes obtained with hexamethylene diisocyanate showed the decrease in the glass transition (T_g) and melting point (T_m) with the increasing length of the diol used. The addition of a tartaric acid derivative modifier (15—16 %) caused an increase in the T_g from -12.8 °C in case of **PUR-PC_1530-HDI** to -5.6 °C for **PUR-PC_1530-T16-HDI**, and from -26.1 to -22.2 °C in



Scheme L

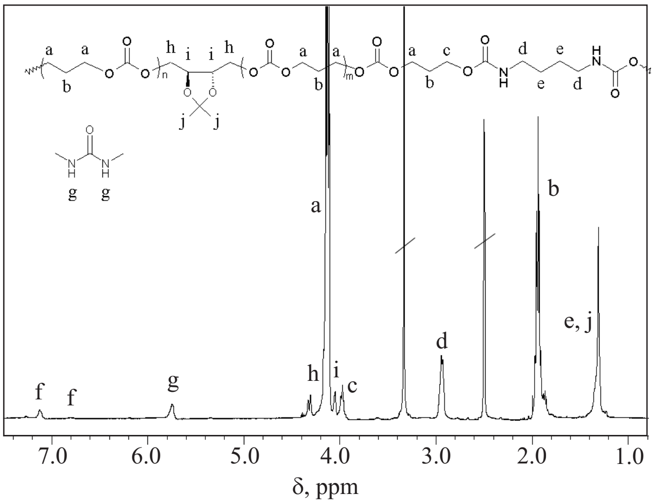


Fig. 2. ^{1}H NMR (400 MHz, DMSO) spectrum of PUR-PC_1530-T8-TMDI

case of **PUR-PC_1680-HDI** and **PUR-PC_1680-T15-HDI**, respectively. In case of polyurethane containing 40 mol % of tartaric acid derivative (**3**) in soft segment (**PUR-BC_T40_2140-HDI**) T_g increased up to -15.9 °C (Table 3).

Polyurethanes based on tetramethylene diisocyanate (TMDI) demonstrated very similar thermal transition temperatures in compare to HDI-based samples. When tartaric acid derivative (**3**) was introduced into polyurethane an increase in glass transition and melting temperatures were observed (Table 3). In case of **PUR-PC_1340-T7-TMDI** the T_g and T_m equal -20.8 and 41.7 °C, respectively, whereas in case of **PUR-PC_1340-T16-TMDI** T_g and T_m increased to -13.6 °C and 57.2 °C, respectively. T_g was also observed to increase with increasing molar mass of modified oligomerol used.

Samples based on isophorone diisocyanate (IPDI) have shown higher values of T_g than HDI and TMDI analogues, for example T_g of **PUR-PC_1530-IPDI**, **PUR-PC_1530-HDI** and **PUR-PC_1530-TMDI** were -7.8, -12.8 and -11.6 °C, respectively. Furthermore IPDI-based samples did not contain crystalline phase.

Thermogravimetric analysis was performed to investigate the influence of the tartaric acid derivative (**3**) incorporation, as well as type of diisocyanate used, on thermal stability of poly(carbonate-urethane). It was found that temperatures at which polyurethane starts to decompose ($T_{5\,\%}$) increase and ranged from 228 to 266 °C within increasing length of the diol used for synthesis of oligocarbonates. The lowest $T_{5\,\%}$ were observed for the samples **PUR-BC_1680-T7-TMDI** and **PUR-BC_1680-T15-HDI** (231 and 235 °C, respectively) containing 7 and 15 mol % of tartaric acid derivative (**3**). The temperature of maximum decomposition rate (T_{max}) also increased with increasing length of diol used for the synthesis oligocarbonates and varied from 300 to 333 °C. Polyurethanes modified by (**3**) as a chain extender **PUR-BC_1680-T7-TMDI** and **PUR-BC_1680-T15-HDI** were characterized by a T_{max} of 300 °C and 310 °C, respectively (Table 3).

Mechanical properties of poly(carbonate-urethane)s

Polyurethanes containing oligocarbonate diols as soft segments were characterized by high elongation at break (ε). Comparing PUR obtained from 1,3-propanediol and 1,4-butanediol it can be noted that the elongation at break was not much different and varies in the range of 650—700 %, while the tensile strength (σ) significantly differs — for **PUR_BC_1900_IPDI** σ = 49 MPa, and for **PUR_PC_1530-IPDI** 15 MPa. Comparing PUR-BC with different molar masses of the soft segment, it can be noticed that in case of **PUR-BC_1680-IPDI** tensile strength and elongation at break were recorded 57 MPa and 650 %, respectively, whereas for **PUR-BC_1900-IPDI** tensile strength of 49 MPa and elongation at break of 700 %. It can be concluded that the higher the molar mass of the soft segment, which is associated with a lower content of hard segments, the elongation at break increases while the tensile strength decreases. Preliminary results indicate that the presence of tartaric acid derivative slightly decreases tensile strength as well as elongation at break of the poly(carbonate-urethane) (Table 3).

T a b l e 3. Thermal and mechanical properties of poly(carbonate-urethane)s

Sample	T_g a), °C	T_m a), °C	$T_{5\,\%}$, °C	T_{max}, °C	δ, MPa	ε, %
PUR-PC_1530-HDI b)	-12.8	50.3	-	-	-	-
PUR-PC_1530_T16-HDI c)	-5.6	57.9	-	-	-	-
PUR-BC_1680-HDI	-26.1	54.7	-	-	-	-
PUR-BC_1680_T15-HDI	-22.2	43.6	235	310	-	-
PUR-BC_T40_2140-HDI d)	-15.9	44.1	-	-	-	-
PUR-PC_1340-TMDI	-22.5	47.7	-	-	-	-
PUR-PC_1340-_T7-TMDI	-20.8	41.7				
PUR-PC_1340_T16-TMDI	-13.6	57.2	-	-	-	-
PUR-PC_1530-TMDI	-11.6	51.9	-	-	-	-
PUR-PC_1530-T8-TMDI	-7.5	f)	-	-	-	-
PUR-BC_1680-TMDI	-24.2	51.2	255	333	-	-
PUR-BC_1680_T7-TMDI	-20.8	41.7	231	300	23±4	420±18
PUR-PBC_1210-TMDI	-7.9	57.2	-	-	-	-
PUR-BC_T3_3710-TMDI	-9.5	53.3	-	-	-	-
PUR-PC_1530-IPDI e)	-7.8	f)	-	-	15±3	510±21
PUR-BC_1680-IPDI	-18.2	e)	-	-	57±10	650±33
PUR-BC_1900-IPDI	-20.5	e)	-	-	49±4	700±20

a) T_g of the soft phase.

b) PUR-PC_1530-HDI — poly(carbonate urethane) based on PC_1530 and hexamethylene diisocyanate (HDI).

c) PUR-PC_1530_T16-HDI — poly(carbonate urethane) based on oligocarbonate diol PC_1530 and hexamethylene diisocyanate (HDI), containing 16 mol % of tartaric acid derivative incorporated as a chain extender.

d) PUR-BC_T40_2140-HDI — poly(carbonate urethane) based on oligocarbonate diol BC_T40_2140 and tetramethylene diisocyanate (TMDI).

e) PUR-PC_1530-IPDI — poly(carbonate urethane) based on oligocarbonate diol PC_1530 and isophorone diisocyanate (IPDI).

f) Melting point was not observed.

CONCLUSIONS

Three methods of introduction of tartaric acid derivative containing two free and two protected OH groups into poly(carbonate-urethane)s chemical structure based on polycondensation, ring opening polymerization (oligocarbonate synthesis step) and polyaddition (as a chain extender — prepolymer synthesis step) reactions were developed. The introduction of tartaric acid derivative into PUR led to slight increase in T_g as well as decrease in decomposition temperatures. Very good mechanical properties of poly(carbonate-urethane)s cured with use of water vapor as a chain extender were slightly worsened when PUR was modified by tartaric acid derivative (**3**). Hydrolytic biodegradation rate of the modified poly(carbonate-urethane)s due to the presence of protected pendent hydroxyl groups, as preliminary results revealed, should be greater than that of unmodified PUR. Such polyurethanes degrade to the naturally occurring putrescine (including saliva) or erythritol, which can be found in fruits, lichens, fungi and fermented food. The results of the biodegradation investigation of the modified poly(carbonate-urethane)s will be presented in future publication.

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