

POLIMERY

Polycarbonate-based polyurethane – attractive materials for adhesives, binders and sealants production

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Abstract: In the last few years, a very wide range of oligocarbonate diols, oligomers of carbonic acid esters terminated on both sides with hydroxyl groups, have appeared on the chemical market. They are mainly used for the production of flexible segments in precious grades of polyurethanes used in biomedical engineering. Poly(carbonate-urethane) due to high resistance to oxidizing and hydrolytic agents is also an attractive material for the production of adhesives and coatings with increased resistance to weather conditions. This paper presents the current state of knowledge on the methods of synthesis and main producers of oligomerols with carbonate groups, methods of poly(carbonate-urethane) synthesis and examples of its commercial applications.

Keywords: aliphatic oligocarbonate diols, isocyanate, polyurethane, mechanical properties, adhesives.

Poliuretany z segmentami oligowęglanowymi jako atrakcyjne materiały do produkcji klejów, spoiw i uszczelnaczy

Streszczenie: W ostatnich latach na rynku chemicznym pojawiła się bardzo bogata gama oligowęglanodiolu, czyli oligomerycznych estrów kwasu węglowego, zakończonych z obu stron grupami hydroksylowymi. Są one wykorzystywane głównie do wytwarzania segmentów elastycznych w szlachetnych gatunkach poliuretanów stosowanych w inżynierii biomedycznej. Poli(węglano-uretany), dzięki dużej odporności na czynniki utleniające i hydrolityczne, stanowią także atrakcyjny materiał do produkcji klejów i powłok, trwałych w różnych warunkach atmosferycznych. W niniejszej pracy przedstawiono aktualny stan wiedzy dotyczący metod otrzymywania i głównych producentów oligomeroli z segmentami oligowęglanowymi, metod syntezy poliuretanów zawierających te segmenty oraz przykłady komercyjnych zastosowań poli(węglano-uretanów).

Słowa kluczowe: alifatyczne oligowęglanodiole, izocyjaniany, poliuretany, właściwości mechaniczne, kleje.

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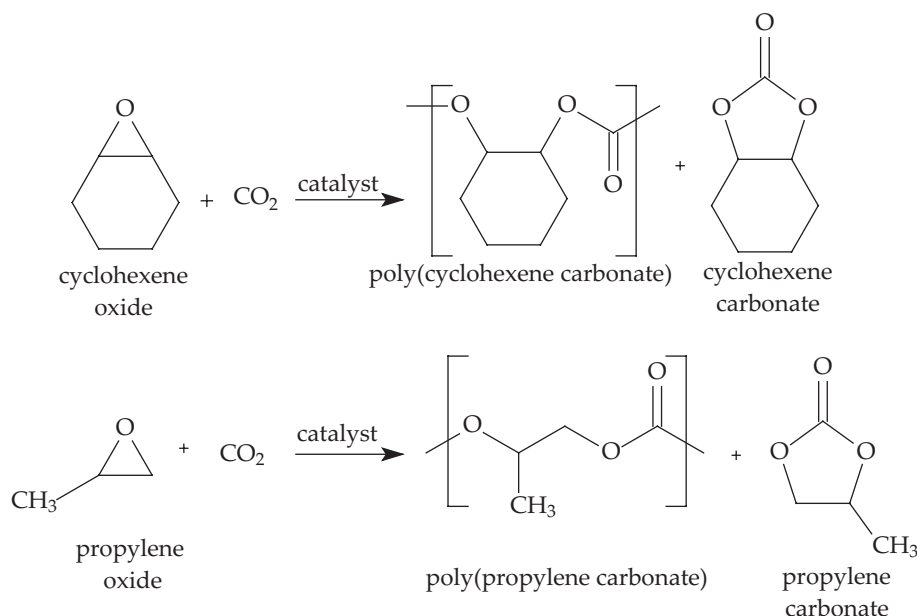
Polyurethanes (PURs) are currently the sixth most widespread group of polymeric materials. It was estimated that PUR demand will grow from 14.2 million tons in 2011 to 22.2 million tons by 2020 [1]. PURs are mainly used for the production of foams, elastomers, adhesives, sealants and coating materials. Their useful properties can be shaped to a very wide extent through the selection of raw materials, synthesis and processing methods, as well as various additives [2, 3]. The major monomers used in the production of PUR are diisocyanates and oligomerols containing at least two hydroxyl groups in their structure. As a result of the reaction of hydroxyl groups with isocyanate ones urethane bonds are formed, and usually the process is carried out so as to obtain, at the first stage, oligomers with isocyanate end groups (urethane prepolymers), which are then used to combine hydroxyl-containing chain extenders into a linear, high molar mass polyurethane [4].

The most commonly used isocyanates are a mixture of isomers of toluilene diisocyanate (TDI) and 4,4'-methylene diphenyl diisocyanate (MDI), as well as some aliphatic derivatives such as a mixture of isomers of 4,4'-methylene dicyclohexyl diisocyanate (HMDI) or hexamethylene diisocyanate (HDI). The type of isocyanate used and the concentration of isocyanate end-groups in the prepolymer have a significant impact on the oligomerol conversion rate, crosslinking and foaming reaction, as well as on some properties of the final product such as flammability or tendency to change of color under the influence of light. However, most of the physicochemical properties of prepolymers and the functional properties of the final products depend on the structure of the oligomerol used, especially the type of their monomeric units, the average length of the segments they form, and the number of hydroxyl end groups. They significantly affect the viscosity of prepolymers, the shape of formed polymers, their mechanical properties, resistance to oxidation and hydrolysis, as well as adhesion to various substrates. In some products, by selecting these segments, a number of other features can be also achieved, such as the ability to form dispersions in water, biocompatibility, resistance to biodegradation and the ability to transport ions, as well as the status of environmentally friendly polymers (by using of vegetable oils and other renewable raw materials for oligomerols production) [5]. Nowadays, oligomerols containing ether moieties obtained in polymerization of propylene oxide or copolymerization of propylene oxide with ethylene oxide occupy a dominant position in the market. They are relatively cheap and are always the first choice for many materials. Their basic disadvantages are the relatively high sensitivity to oxidation and low polarity of ether segments, which limit the possibilities of their use in the production of materials with high mechanical strength and high adhesion to many substrates. In order to improve these parameters, some more polar ester units are introduced into the PUR structure, but this strategy also has some limitations due to the high susceptibility

of ester bonds to hydrolysis. An interesting alternative is the use of carbonate oligomerols as polar segments, which have a much higher hydrolysis resistance than polyesters. These types of raw materials are still quite expensive and for a long time they were used mainly for the production of PUR used to manufacture medical implants. However, recently a number of new methods of obtaining carbonate oligomerols from safe, cheap and environmentally friendly raw materials have appeared, which has contributed to the rapid increase in the scale of their production and the development of technologies to compose noble grades of PUR coating materials, adhesives and elastomers. In this paper, we present the current state of knowledge in this area of polymeric materials, including many original solutions that have arisen in the Chair of Polymer Chemistry and Technology at Warsaw University of Technology.

SYNTHESIS OF OLIGOCARBONATE DIOLS

Oligocarbonate diols belong to the group of oligomerols that act as soft segment in the PUR structure [6]. They are resistant to the hydrolysis and oxidation. Additionally, the great advantage of oligocarbonate diols compared with oligoesterols is the absence of acidic degradation products during the *in vivo* degradation. Aliphatic polycarbonates can be obtained by several methods. The oldest one is based on the condensation of diols with phosgene. However due to the high toxicity of phosgene, and large amount of salts produced during the reaction, alternative methods are still developed. In recent years, a lot of attention has been paid to carbon dioxide, which is nontoxic, cheap and available from renewable resources [7]. Direct synthesis of polycarbonates from CO₂ can be conducted by copolymerization reaction with oxiranes or oxetanes as well as polycondensation with diols [8]. The most studied oxirane monomers are propylene oxide (PO) and cyclohexene oxide (CHO), both used in the industrial scale (Scheme A) [9]. In this reaction, using cobalt [10], organoaluminum and zinc catalysts it is possible to obtain linear aliphatic polycarbonates with molar mass up to 500 000 g/mol and small amount of cyclic carbonate [11]. To lower the molar mass of polymer, the alcoholysis with 1,4-butanediol and 1,6-heksanediol is required. The copolymerization reaction of PO or CHO with CO₂ can be performed also under metal-free conditions, using triethyl borane for the activation of epoxide and onium halides or onium alkoxides containing either ammonium, phosphonium, or phosphazanium cations to initiate the copolymerization [12]. Moreover, it was proved that copolymerization with the CHO-based functional monomers gives polycarbonates with higher glass temperature than in the case when the propylene oxide is utilized [13]. The direct condensation of diols and CO₂ can be carried out in the presence of the CeO₂/2-cyanopyridine or CeO₂/2-furonitrile catalyst system [8]. The obtained polycarbonate was character-



Scheme A

ized by molar mass up to 5000 g/mol and that could be controlled by adjusting the concentration of diols and 2-furonitrile.

In the copolymerization of epoxides with CO₂ besides pure oligocarbonate diols also oligo(ether-carbonate) diols (OECD) can be produced. Such oligomerols find use in polymers with remarkable properties, such as plastics with improved compatibility with CO₂ blowing agents and fire-resistant foams. Haider *et al.* [14] patented a number of oligo(ether-carbonate) diols made by copolymerization of CO₂ with a starter molecule (diol, oligomerol, alkoxyated oligomer of glycol) and an alkylene oxide, in the presence of a “substantially non-crystalline double metal cyanide catalyst” (such as a zinc hexacyanocobaltate/*t*-butyl alcohol complex prepared with a specific procedure to obtain a low-crystalline catalyst), wherein the resultant oligomerol has an incorporated CO₂ content up to 40 wt %. Among the advantages claimed are the low levels of by-products (cyclic carbonates). Bayer Material Science and Bayer Technology Services, in collaboration with the RWTH University of Applied Science in Aachen (Germany) and RWE Power have developed a process for oligo(ether-carbonate) diols from CO₂. The project, named “Dream Production”, has led to the building of a pilot plant where OECD is produced on a kilogram scale [15]. The oligomerols consumption was about 6 Mt/a in 2003.

The synthesis of oligocarbonate diols from five-membered cyclic carbonates and α,ω -diols leads to oligomer without ether groups having molar mass up to 3 000 g/mol [16]. The diols used in the reaction must contain at least 4 carbon atoms in the molecule since the ones with shorter chains distill with azeotrope agent and promote the ether group formation in the oligomer chain. The most commonly used catalysts are Bu₂SnO [16] and alkali metal salt [17]. However, the potential toxicity of

tin catalyst residues in the final product is a concern when it comes to their biomedical application. Moreover, tin catalysts promote side reactions during PUR synthesis, giving cross-linked products. Another possibility to obtain oligocarbonate diols from cyclic carbonates is ring-opening polymerization of trimethylene carbonate (TMC) initiated by diols. The reaction can be conducted at the temperature above 100°C without a catalyst [18], as well as at 30°C in the presence of organocatalyst or 70°C using trimethylglycine (TMG) [19, 20]. In the first case, when the thermal (spontaneous) polymerization was conducted, the molar mass of polymer reached 200 000 g/mol, and could be controlled by the diol/TMC ratio. The reaction catalyzed by TMG gives oligodiols with molar mass about 4000 g/mol and low dispersity. Moreover the catalyst is environmentally friendly, as naturally occurring in the plant and human body.

Polycarbonate synthesis based on non-toxic green reagents can be also conducted by transesterification between organic carbonate [dimethyl carbonate (DMC), diethyl carbonate] and diols in the presence of different types of homogeneous and heterogeneous catalysts such as lithium acetylacetonate (LiAcac) [21], sodium acetylacetonate (NaAcac) [22], dimethylaminopyridine [21], NaH [23], KNO₃/Al₂O₃ [24], metal-organic frameworks [25] and layered double hydroxides [26]. Due to the fact, that during reaction the substrate co-distills with the low molar mass by-product, the final oligocarbonate is end-capped with both the hydroxyl and alkylcarbonate groups. The alkylcarbonate ends are not active in the reaction with diisocyanate, and the PUR with low molar mass is achieved. To solve this problem the reaction can be conducted in two steps process followed by reacting of diol with a high molar excess of DMC and then subjecting the intermediate product, [hexamethylene bis(methylcarbonate)], to the reaction with the appropri-

ate diol [27]. The synthesis was performed in the presence of 1,4-dioxane.

SYNTHESIS OF PUR BASED ON OLIGOCARBONATE DIOLS

Synthesis of poly(carbonate-urethane)s

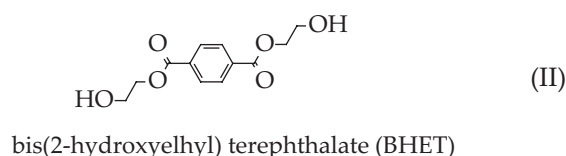
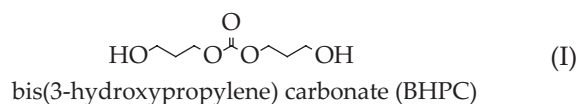
Poly(carbonate-urethane)s (PCUs) obtained with the use of MDI, dibutyltin dilaurate (as a catalyst), and 1,4-butanediol (as a chain extender) were described by Kim *et al.* [28]. Reactions were carried out in solution (dimethylacetamide). The molar ratio of polyol, diisocyanate, and the chain extender was equal to 1:2:1, respectively (38 wt % of hard segments). The oligocarbonate diols based on (i) 1,6-hexanediol, (ii) 1,6-hexanediol (50%) and 1,4-butanediol (50%), (iii) 1,6-hexanediol (40%), 1,4-butanediol (40%), 3-methyl-1,5-pentanediol (20%), as well as (iv) oligo(tetramethylene ether) glycol were used as the soft segment precursors. It is worth mentioning that the presence of methyl side groups from 3-methyl-1,5-pentanediol resulted in a better transparency of the final PCUs and decreased degree of microphase separation, due to a better miscibility of the soft and hard segments. Interestingly, a usage of oligocarbonate diols containing several various types of diols led to decrease the crystallinity degree, related to a less regular structure of the product. The tensile strength and elongation at break of the obtained PCUs were equal to 44–65 MPa and 440–680%, respectively. The poly(ether-carbonate-urethane) based on poly(tetramethylene ether) glycol was characterized by much lower tensile strength (10 MPa), a similar value of elongation at break (650%) and the lowest value of glass transition temperature (T_g) compared to PCUs [28]. Furthermore, other diols such as 1,3-propanediol, 1,5-pentanediol, 1,4-pentanediol could be also used in PUR synthesis, however, the PUR based on 1,4-butanediol exhibited better mechanical properties [29]. It is related to the fact that in case of 1,4-butanediol, the hard segments can form well-ordered structures and crystals because of the efficient hydrogen bonding [28, 30]. The increase of the number of methylene groups in the main chain of PCUs or presence of branches in the chain extender molecules leads to a decrease of the glass transition temperature, and to higher chain flexibility. Chain extenders with odd numbers of methylene groups or branches decrease the PUR's crystallinity and degree of ordering [29].

The ultra-soft thermoplastic PCUs (23 wt % of hard segments, with a Shore A hardness of 64) based on methylene bis(4-cyclohexylisocyanate), 1,4-butanediol, and oligocarbonate diols ($\bar{M}_n = 2000$ g/mol) derived from 1,6-hexanediol and 2-methyl-1,5-pentanediol have been reported by Kull *et al.* [31]. Polymers were prepared by the quasi-prepolymer technique, which allows better control of the soft and hard segment. In comparison to a ordering to common prepolymer method this new technique utilized the addition of a small amount of macrodiol containing low-molec-

ular weight oligomers as a chain extender in stoichiometric ratio to the urethane prepolymer. Synthesis was carried out without solvent with the use of tin(II) 2-ethylhexanoate as a catalyst. The resultant polymer was cured in an oven at 107°C for two hours and next post cured at 93°C for several days to the complete disappearance of the isocyanate absorption band at 2264 cm⁻¹ in the FT-IR spectra [31].

Kojio *et al.* have carried out the PCUs synthesis based on MDI, aliphatic oligocarbonate diol with different numbers of methylene groups (3–10), and 1,4-butanediol as a chain extender [32]. The molar ratio of NCO to total number of the OH groups was equal to 1.03–1.05. After mixing of the reactants, reaction was carried out at 80°C for 5 min and then viscous mixture was placed in the centrifugal mold at 110°C and kept at this temperature for 12 h. After removing from the centrifugal mold, the product was postcured at 100°C for 24 h. The glass transition temperatures of the resultant PCUs were in the range of -27 to -7°C depending on the number of methylene groups in soft segments. The tensile strengths of obtained PUR at $T = T_g + 50^\circ\text{C}$ were equal to 15–38 MPa [32].

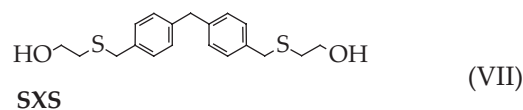
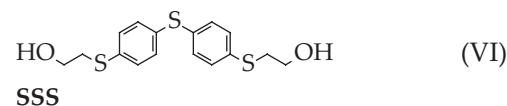
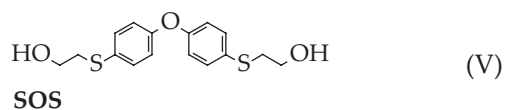
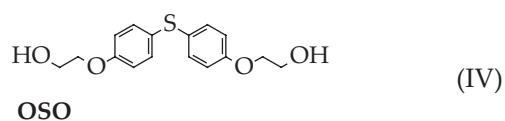
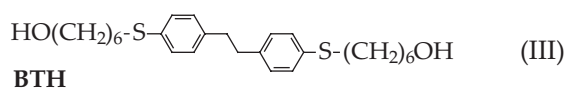
The PCUs based on HMDI, oligo(hexamethylene carbonate) diol ($\bar{M}_n = 860$ g/mol), and the newly synthesized cleavable carbonate chain extender [bis(3-hydroxypropylene) carbonate] (BHPC) were obtained by Ehrmann *et al.* [33]. According to current reports, oligo(trimethylene carbonate) shows fast but controlled degradation, therefore the usage of its countertype – BHPC as a degradable hard segment of PUR was presented [34]. Other chain extender bis(2-hydroxyethyl) terephthalate (BHET) was also used. The structures of BHPC and BHET are shown at Formula (I) and Formula (II).



The syntheses of PUR were carried out in two steps. First, the urethane prepolymer was obtained from macrodiol, HMDI and tin(II) 2-ethylhexanoate as a catalyst in dry dimethylformamide (DMF) under argon atmosphere. After 3–4 h of mixing at 50°C, chain extender dissolved in dry DMF was added to reaction mixture and the reaction was continued at 50°C overnight to complete the polyaddition. Finally, product was diluted with DMF and precipitated in excess of methanol (80–90% yield). The molar ratios of diisocyanate, macrodiol, and chain extender used in the synthesis were equal to 3:1:2 or 2:1:1. The authors have proved that hard block degradation was limited thanks to the presence of carbonate units in chain extender. The crucial advantage of PCUs is the fact that degradation of carbonate moieties (in hard segments too) does not followed

acidic and autocatalytic degradation mechanism, therefore inflammatory response in the surrounding tissue should be significantly decreased [33]. The resultant PUR based on BHPC and BHET was characterized by high elongation at break ($\epsilon = 900\%$), except for one sample containing 50 wt % of hard segment ($\epsilon = 60\%$). Presence of stiff BHET moieties resulted in the highest tensile strength of 13 MPa. The hydrolytic degradation of BHPC-based PUR was faster than in case of PUR containing BHET as a chain extender (equal content of hard segments), which confirmed the ability of the carbonate-based hard segments to degrade [33, 35].

The properties of PCUs can be modified by introduction of large, sulfur-containing chain extenders to the structure of PURs. Examples of such chain extenders are 4,4'-(ethane-1,2-diyl)bis(benzenethiohexanol) (BTH) [36], 2,2'-[sulfanediylbis(benzene-1,4-diylloxy)]diethanol (OSO) [37], 2,2'-[oxybis(benzene-1,4-diylsulfanediyl)]diethanol (SOS) [37], 2,2'-[sulfanediylbis(benzene-1,4-diylsulfanediyl)]diethanol (SSS) [37], and 2,2'-[methanediylbis(benzene-1,4-diylmethanediylsulfanediyl)]diethanol (SXS) [38] [Formulas (III)–(VII)]. The advantages of their application are higher thermal stability and better mechanical properties with simultaneously enhanced adhesion to metals compared to PURs obtained with aliphatic chain extenders [37, 39]. It is worth mentioning that the sulfur-based PUR exhibited twice higher adhesive strength to copper than those based on 1,4-butanediol [36]. The refractive index and adhesive strength increased with the increase of the content of sulfur atoms in the polymer chain [37]. The PCUs based on oligo(hexamethylene carbonate) diol (860 g/mol), MDI (molar ratio of NCO to OH = 1), and different chain extenders (OSO, SOS, SSS) showed high glass transition temperatures (10–46°C) and low degree of microphase separation. The PUR based on OSO, SSS, and SOS exhibited tensile strength of 50–52 MPa, 38–40 MPa, and 29–37 MPa, respectively. The elongation at break of all samples was in the range of 200–325% [37]. A change of the chain extender to BTH ratio resulted in PURs exhibiting tensile strength, elongation at break, and glass transition temperature of 41–51 MPa, 130–360%, 12–37°C, respectively [36]. In case of the use of MDI, oligo(hexamethylene carbonate) diol (2000 g/mol) and SXS, showed tensile strength, elongation at break, and glass transition temperature of -9 to -8°C, 27–32 MPa, and 450–550%, respectively [38].



The other example of the synthesis of PCU is the one-step bulk polyaddition presented by Oh *et al.* [40]. In the mentioned article, bio-based thermoplastic PUR elastomers were obtained from isosorbide, oligocarbonate diol (2000 g/mol), and HMDI (molar ratio = 1 : 1 : 1.05) without a catalyst. Isosorbide is an eco-friendly, non-toxic, chemically and thermally stable diol, which can be produced from starch. Isosorbide-based PURs are characterized with a more rigid structure due to a presence of two cycloaliphatic rings in isosorbide molecule [41, 42]. After the solid oligomerol and isosorbide were melted, HMDI was added and stirred under nitrogen flow for five minutes. The reaction mixture was placed in a Teflon® beaker and kept without mixing at 120°C until the reaction was over (12 h). After precipitation in isopropyl alcohol and purification in methanol the product was dried at 50°C for 24 h under vacuum. Isosorbide has a more hydrophobic structure than other reactants, therefore, it shows weaker miscibility with macrodiols and diisocyanates. Hence, the best molar ratio of isosorbide to oligocarbonate diol has been determined as 1 : 1. The resultant PUR exhibited glass transition temperatures in the range of -38 to -34°C, tensile strength and elongation at break 14–54 MPa and 950–1800%, respectively [40].

Similar isosorbide-based PURs obtained from poly(tetramethylene ether) glycol instead of carbonate diols were published by Kim *et al.* [43]. These poly(ether-urethane)s exhibited much lower glass transition temperature (-48 to -39°C) than their carbonate-based analogues. The optimal molar ratio of isosorbide to polyether was 1 : 1, which gave PUR with elongation at break of 1600% and tensile strength of 18 MPa. Both, the isosorbide-based poly(carbonate-urethane) and poly(ether-urethane) are degradable polymers, which can be used in a biomedical engineering [43].

The other examples of the eco-friendly compounds used in PUR synthesis are chitin [44–46], chitosan [47–49], starch [50, 51], cellulose [50], glucose [52], sucrose [52], mannitol [52], and sorbitol [52]. The introduction of these molecules as chain extenders or cross-linking agents to PUR structure enhanced biocompatibility and biodegradability of PURs for potential applications such as drug delivery systems [50]. The mechanical, thermal, and sorption properties of PUR could be improved by choosing the suitable type of polyols, isocyanates, and optimal molar ratio of NCO to OH groups [50, 52].

Examples of commercially available oligocarbonate diols and oligocarbonate-based urethane prepolymers are ETERNACOLL® and ETERNATHANE® (supplied by UBE), respectively. UBE presented a novel poly(ether-

carbonate-urethane)s internal coatings for pipelines with improved durability, mechanical properties, and resistance for abrasion and hydrolysis. Those coatings were synthesized by mixing of oligo(tetramethylene ether) glycol ($\bar{M}_n = 1000$ g/mol), oligo(hexamethylene carbonate) diol (ETERNACOLL® PH50, $\bar{M}_n = 500$ g/mol) (40 and 60 wt %, respectively), polymeric MDI (SUPRASEC® 2416), and 1,4-butanediol in a one-pot process. The molar ratio of NCO to OH was equal to 1.2. It was found that addition of oligocarbonate diols improves the abrasion resistance, mechanical properties, and hydrolytic stability, and prevents loss of mechanical properties after hydrolytic degradation of the investigated PUR coatings [53].

Synthesis of poly(carbonate-urethane-urea)s

Mazurek *et al.* proposed a water-cured poly(carbonate-urethane-urea)s (PCUUs) based on oligocarbonate diols ($\bar{M}_n \approx 2000$ g/mol) and explored the influence of the hydrocarbon chain (soft segment) length on their properties [54]. PCUUs were synthesized from isophorone diisocyanate (IPDI) and polyol in molar ratio of 3 : 1 at 80°C under nitrogen atmosphere without a catalyst and a solvent. The chain extending process of urethane prepolymer by water vapor was investigated in a climatic chamber under the following temperature and humidity regime: 3 days at 70°C, 10% of humidity, 1 day at 70°C, 20% of humidity, and 3 days at 60°C, 40% of humidity. Even though the curing process was investigated without a catalyst at the temperature lower than 80°C, the allophanate and biuret linkages were present in final product. Thus, the resultant PCUUs were not soluble in common solvents. The number of methylene groups in carbonate oligomerols strongly influenced thermal and mechanical properties of PUR. The increase of hydrocarbon chain length between carbonate groups led to the increase of elasticity (decrease of glass transition temperature) and crystalline phase content. The authors have found that decrease of hydrocarbon fragments concentration caused decrease of permeability for water vapor, thus curing process lasted longer. As a consequence, the reaction between isocyanate groups and urethane/urea fragments led to the increase of the number of allophanate and biuret groups' concentration in case of samples with lower number of methylene groups. The obtained PCUUs showed high tensile strength up to 40 MPa with simultaneous elongation at break of 400–600%, depending on the type of carbonate oligomerols. The moisture-cured PCUUs exhibited good abrasion resistance, thermal stability, and good adhesion to various surfaces. Those interesting features resulted from the creation of the covalent cross-linking during curing process [54–57].

PCUs and PCUUs are auspicious implant materials, because of hydrolytic resistance and higher biocompatibility than poly(ester-urethane)s. It is worth mentioning that poly(carbonate-urethane-urea)s based on oligo(alkylene carbonate) diols containing 6, 9, 10, or

12 methylene groups in hydrocarbon chains exhibited good hydrolysis resistance for 10 weeks. In the presence of enzymes like cholesterol esterase PCUUs degrade, but this process is much slower compared to poly(ether-urethane)s and poly(ester-urethane)s hydrolysis [58, 59].

Water-cured PCUUs based on oligo(alkylene carbonate)s (C9, C10, C12; $\bar{M}_n = 2100$ –3800 g/mol) and lysine ethyl ester diisocyanate were presented as shape-memory materials with recovery ratio of *ca.* 99%. Additionally, these PCUUs exhibited 22–28 MPa tensile strength and *ca.* 1000% elongation at break [60].

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

Mazurek *et al.* presented PUR based on oligocarbonate and oligo(ester-carbonate) diols with a molar mass of 1500–3000 g/mol [61]. The syntheses were carried out according to the previously presented procedure [54]. Oligo(tetramethylene carbonate) diol, oligo(pentamethylene carbonate) diol or poly(pentamethylene adipate-*co*-carbonate) diol, poly(tetramethylene succinate-*co*-carbonate) diol and poly(pentamethylene succinate-*co*-carbonate) diol with different contents of carbonate units (43–57 mol %) were used as oligomerols and IPDI or HMDI as isocyanates. The obtained poly(ester-carbonate-urethane-urea)s (PECUUs) exhibited higher elongation at break and lower glass transition temperatures than poly(carbonate-urethane)s. In case of the use of IPDI amorphous polymers were obtained, whereas introduction of HMDI led to more crystalline structures. All of the obtained polymers showed similar melting points (39–46°C) and exhibited relatively high tensile strengths 17–50 MPa and elongations at break of 300–800% [61].

Biodegradable PECUUs based on oligo(tetramethylene succinate-*co*-carbonate) diols ($\bar{M}_n = 2600$ –3700 g/mol), IPDI or HMDI were synthesized from tetramethylene bis(methyl carbonate), dimethyl succinate, and 1,4-butanediol according to the method described earlier [58]. PUR based on oligoesterols such as oligo(glycolic acid), oligo(ϵ -caprolactone), oligo(lactic acid) are susceptible to hydrolytic biodegradation, though oligoester fragments are source of crystalline phase. In case of presence of crystalline phase in PUR structure, biodegradation is limited. Aliphatic polycarbonates show a weak tendency to biodegradation and reduced ability to crystallization. Hence, the authors have found optimal content of carbonate units in oligo(tetramethylene succinate-*co*-carbonate) diols (57–74 mol %), which made the obtained macrodiols amorphous. The resultant PUR exhibited glass transition temperature in the range of -36 to -29°C. Furthermore, PUR based on HMDI showed higher elasticity than those synthesized from IPDI for equal content of carbonate units. The PECCUs made of IPDI were amorphous, whereas those obtained from HMDI exhibited low degree of crystallinity. The hardness of the PECUUs was in the range of 60–80°Sh A and 20–35°Sh D. In case of the use

of HMDI, the products exhibited hardness and tensile strength higher by 14–26% and 10–50%, respectively, than in case of IPDI. The obtained materials showed excellent tensile strength up to 60 MPa and elongation at break about 500%. The preliminary results of the biodegradation proved that PECUUs containing 40–65 mol % of carbonate units in soft (amorphous) segments undergo hydrolytic and enzymatic degradation – weight loss after 7 months was equal to about 20% [62–65].

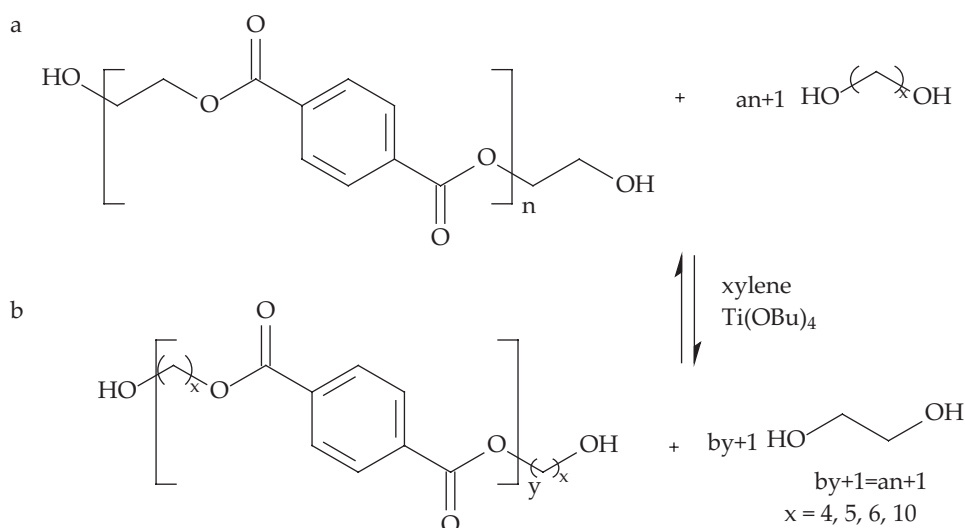
The same materials were investigated by Mystkowska *et al.* as potentially attractive for application in tissue engineering [66]. Besides, oligo(alkylene succinate-*co*-carbonate) PECUUs were synthesized from oligo(alkylene adipate-*co*-carbonate) diols. Elastomers based on the adipic acid derivatives exhibited lower glass transition temperature, higher elongation at break, and higher tensile strength in comparison to the succinate acid derivatives. The resultant elastomers exhibited tensile strengths and elongations at break equal to 20–58 MPa and 500–750%, respectively. Hydrophilic structure of PUR increases water penetration and hydrolysis rate, especially in case of IPDI usage, which was confirmed based on water sorption and hydrolysis tests. The authors revealed that PECUUs based on IPDI showed anti-biofilm properties. The hemolysis was observed in the range of 3–10% for the majority of tested samples, thus their hemocompatibility was high. The obtained poly(ester-carbonate-urethane-urea)s were used as supports for growing of human keratinocytes HaCaT on their surfaces coated with collagen. However, the authors underlined that further research concerning influence of PUR structure on biological properties is necessary to confirm applicability of PECUUs in tissue engineering [66].

The promising aliphatic-aromatic PECUUs elastomers based on poly(ethylene terephthalate) (PET) waste and dimethyl carbonate as source of ester and carbonate units, respectively, were obtained [67]. The authors developed a new synthesis method of alcoholysis of oligo(alkylene terephthalate) diols by PET waste using

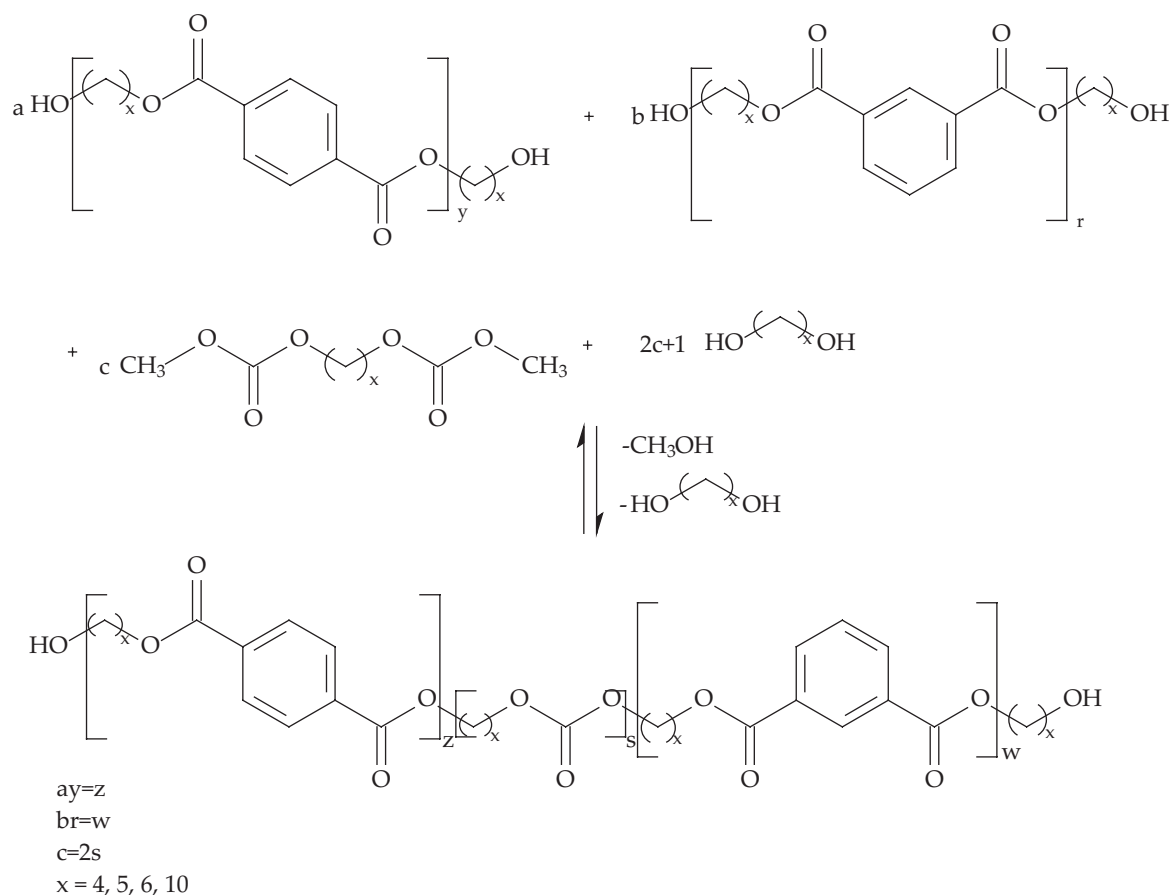
different diols and xylene as an azeotropic solvent at 180–210°C (Scheme B). The synthesis method of aliphatic-aromatic oligo(ester-*co*-carbonate) diols is presented at Scheme C. PECUU elastomers were synthesized by the prepolymer method using three-fold excess of diisocyanates (IPDI or HMDI) and water vapor as a chain extender. It should be mentioned that the occurrence of aromatic rings in the soft segments of oligomerols caused increase of mechanical strength and thermal resistance of PUR. The presence of aromatic-aliphatic esters and aliphatic carbonates in PUR structure provided better hydrolysis resistance, better mechanical and thermal properties than those obtained for PURs synthesized based on oligoesterols alone. In addition, the presence of aliphatic carbonate units provided unique elastomeric properties to these materials, resulting in tremendous tensile strengths (up to 60 MPa) with simultaneous high elongation at break (320%). Elastomers based on IPDI demonstrated higher tensile strength, lower elongation at break, and higher glass transition temperatures in comparison to those derived from HMDI, due to a more rigid structure of IPDI. The elastomeric properties of the synthesized PUR were maintained up to 44% content of aromatic units in the oligo(ester-carbonate) diols in case a mixture of terephthalate and isophthalate fragments was utilized. Furthermore, an introduction of PET waste to PECUU structure resulted in a higher thermal stability than those of aliphatic oligocarbonate diols [67].

APPLICATION OF OLIGOCARBONATE-BASED PUR

Literature sources estimate the size of the global oligo-carbonate diol (OCD) market at USD 182–200 million (data for 2019). In the next 5 years (until 2025), a steady increase in demand for this type of compounds is expected, characterized by CAGR (Compound Annual Growth Rate) values of 3–5% [68, 69]. It is expected that strong development of this segment of the chemical market will be stim-



Scheme B



Scheme C

ulated mainly by the increase in demand in the APEC countries (Asia-Pacific), which already account for almost half of the global demand for OCD (followed by North America and Europe) [69].

Major OCD manufacturers include companies such as UBE Industries, Ltd. (products of the ETERNACOLL® family), Mitsubishi Chemical Corporation (obtained from castor oil BENEbIOL™), Asahi Kasei Corporation (DURANOL™), Covestro AG [OCD and oligo(ester-carbonate) diols from the Desmophen® C and Cardyon® series], Tosoh Corporation (OCD with the trade name NIPPOLAN®), Daicel Corporation (OCD series with the trade name PLACELL CD™), Perstorp Group (diols with the trade name OXYMERTM™, Saudi Aramco (oligomers from the CONVERGE® family obtained from propylene oxide and CO₂), GRR Fine Chem Pvt. Ltd., Caffaro Industrie (oligocarbonate diols from the Ravecarb family) and Cromogenia Units (ROPOL PC) – many of them are simultaneously producers of PUR (e.g. UBE, Asahi Kasei, Covestro AG)[69].

In the chemical industry, oligocarbonate diols (OCDs) are mainly used in the synthesis of high-quality PUR, which are then intended for composing, among others, the film-forming and adhesive materials and elastomers [69]. Of course, a number of factors influence the type of PUR applications containing OCD segments (e.g. car-

bonate content and type of glycol residues in macromolecules, polymer chain architecture, degree of crystallinity and physical state of OCD), however, for ecological reasons, one of the most important is the possibility of reducing the so-called carbon footprint by chemical binding of carbon dioxide (OCD synthesis by copolymerization of CO₂ with alkylene oxides) [69]. A PUR life cycle analysis of PURs based on poly(propylene carbonate) and poly(ethylene carbonate), in which CO₂ is 40–50% by weight, indicates a reduction in the demand for fossil resources by 13–16% and greenhouse gas emissions by 11–19% compared to products based on the polyether diols used so far [70, 71].

Due to the change in consumer preferences (increased awareness of ecological threats) and legal restrictions related to the protection of animals and the emission of volatile organic pollutants (VOCs) among the industrial uses of polyurethanes based on OCD, the production of synthetic substitutes for natural (animal) leather is becoming more and more important. It is expected that in the coming years this market segment will be one of the two main factors responsible for the increase in a global demand for solid OCDs [69]. In the production of artificial leather, poly(urethane-carbonate)s can act as structural components responsible for the mechanical properties of the final product [72]: their solutions in an organic

solvent (most often in toxic DMF) are used to impregnate nonwovens and knitted fabrics [72–74], although the research on the use of water-based systems for this purpose are carried out as well [75]. PURs comprising OCD segments are also contained in some of the finishing coatings applied to the surface of impregnates in order to provide them with appropriate aesthetic parameters (leather-like appearance) [75, 76]. Products made of synthetic leather prepared in such a way are widely used in the automotive, footwear and textile industries [69, 72].

An important segment of applications of PURs based on the solid OCD are coat-forming materials [69]. Because of the economic and ecological reasons (minimizing VOC emissions, eliminating costly organic solvents), as well as the excellent properties of the coatings obtained, water-borne PUR and poly(urethane-urea) systems are being intensively developed, in which OCD completely or partially replaces classic oligomerols [77–83]. The introduction of the OCD segments to PUR chains increases their oxidative stability (relative to PURs based on oligoetherols) and hydrolytic stability of coatings (compared to PURs based on oligoester diols) [70, 38, 84], and the presence of polar carbonate groups increases their adhesion to the substrate and improves mechanical parameters [81, 84, 85]. From the point of view of modification of the properties of the obtained protective layers, an important advantage of the systems based on aqueous dispersions of poly(carbonate-urethane)s is their ability to an easy incorporation of various additives, including nanofillers (synthesis of composite coatings) [78, 86] and perfluorinated polymers (coatings with reduced surface free energy) [87].

The excellent adhesive properties of PURs and poly(urethane-urea)s containing flexible OCD segments make them a promising group of intermediates in the synthesis of modern adhesive materials – adhesives and sealants. The fact that these polymers simultaneously exhibit the properties of elastomers and thermoplastics [38, 88, 89] allows their application in the field of reactive hot-melt adhesives (RHMA) [70, 90]. Such systems at room temperature are semi-crystalline solids that require heating above 100°C before the application (utilizing the thermoplastic features). The formation of a flexible joint occurs quickly during the cooling and its final mechanical parameters are achieved as a result of much slower chemical cross-linking (a catalytic reaction of the isocyanate groups of the urethane prepolymer with moisture) [70, 90]. Some recent studies have shown that the presence of carbonate groups in RHMA promotes an increase in the adhesion of the seam to metallic surfaces (steel, aluminum) both before and after a chemical curing, and moreover such seams have better parameters than their analogues made of a commercial RHMA [91]. The similar effect is observed when bonding surfaces are made of the other types of materials, *e.g.* polymers (PMMA, polycarbonates) as well as leather and styrene-butadiene rubber that are used in a footwear industry [92, 93]. It is worth

noting that OCDs or their blends with other oligodiols (*e.g.* those from biomass processing), can be used as oligomerols components, *e.g.* from biomass processing for the synthesis of PURs-based RHMA [94].

Liquid carbonate-urethane prepolymers terminated with NCO groups may find application as the reactive one-component adhesives, in which the seam is formed as a result of reaction with proton-donor moieties present on the joined surfaces and/or cross-linking due to moisture [54, 61, 90]. Contrary to RHMA, their application is carried out at room temperature, which is a significant advantage of this type of systems. The elastic coatings obtained after the cross-linking process are characterized by an increased resistance to hydrolysis [58], while the introduction of aromatic moieties (*e.g.* PET recyclates) improves mechanical parameters as well as thermal and oxidative stability [67]. Reactive, one-component PUR adhesives are intensively studied, for instance the problem of blistering in these systems (the adverse effect of the evolution of CO₂ which is a by-product of the curing process) may be minimized by application of silane modifiers [95] or latent cross-linking agents based on oxazolidine [96]. Also in Poland, such works are carried out and the good example is the project named CARBOPUR implemented by the researchers from the consortium of Warsaw University of Technology and Rzeszów University of Technology carried out as part of the SYNCHEM research program [97].

Among the potential applications proposed for the PURs containing flexible oligocarbonate segments, biomedical applications should also be mentioned, because they exhibit excellent mechanical properties and biocompatibility [98, 99]. Work in this area is still at the stage of basic research, it can be expected that in the near future they will scale up into industrial practice. Agnol *et al.* proposed the use of PURs based OCD manufactured by UBE (ETERNACOLL® series) as a safe (low cytotoxicity, high cell proliferation) tissue binder used in the surgical treatment of intervertebral disc hernia [100]. In the case of vascular surgery, PURs with oligo(carbonate-urea) segments may be interesting materials for the production of vascular grafts with reduced susceptibility to thrombus formation [101–103], as well as cellular scaffolds used in tissue engineering [66, 104]. The biocompatibility of poly(carbonate-urethane)s, their resistance to degradation in the body and low cytotoxicity can be used in the production of implants [105–107]. These materials can also be used to coat the surface of medical devices that come into contact with blood with a layer that prevents the deposition of thrombocytes [108] or the growth of microorganisms and fungi [39]. One of the latest ideas for the use of poly(carbonate-urethane)s in medicine is the production of hydrogels with very good affinity for living cells and biological tissues [109].

Research on poly(carbonate-urea-urethane)s containing aliphatic oligocarbonate blocks and exhibiting memory shape is currently underway [60, 110]. It should be

expected that such systems will find a wide application in the area of smart materials *e.g.* for biomedical purposes.

SUMMARY

Poly(carbonate-urethane)s obtained from OCD exhibit excellent mechanical properties such as a high tensile strength, elongation at break and abrasion resistance. Additionally, the usage of OCD provides a good hydrolysis resistance, oxidative stability and good adhesion to many materials. Although the production of these oligomerols has been growing rapidly in recent years, their price is still high and it seems to be a barrier to the commercialization of new PUR materials. In addition, these oligomerols are highly viscous, which makes it difficult to prepare their compositions with some fillers. For this reason, they are very often used in compositions with the mass-produced oligomerols to give products with the properties acceptable to future users. In Poland, such work is currently carried out by a consortium formed by the employees of the Warsaw University of Technology and the University of Technology in Rzeszów as part of the project named CARBOPUR within the program co-financed by the National Center for Research and Development and Synthos Ltd. The project will result in the elaboration of a method of manufacturing of a few types of one-component adhesives capable of bonding of various types of materials (metals, glass, some types of plastics). The basic components of these systems will be PUR adhesives and sealants cured with moisture from the air. In order to achieve joints of good mechanical properties and high resistance to atmospheric factors, a new type of oligomerols containing carbonate groups and aliphatic-aromatic ester groups derived from PET wastes will be utilized for the preparation of urethane prepolymers. The aim of further studies will be to change the curing mechanism of prepolymers in such a way, that the hydrolysis of isocyanate groups resulting in CO₂ evolution and blistering of joints will be eliminated. To assure the appropriate rheological properties and improved chemical resistance as well as some other functional parameters, the urethane prepolymers will be modified with appropriate plasticizers, fillers, pigments, surfactants and UV stabilizers.

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