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POLIMERY

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII i PRZETWÓRSTWU POLIMERÓW

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Recent advances in the synthesis and applications of poly(1,4-dioxan-2-one)based copolymers

Summary — The review provides the recent advances in the synthesis, properties and applications of poly(1,4-dioxan-2-one) (PPDX). PPDX represents a promising candidate as a biodegradable substitute, because of its interesting thermomechanical properties such as a melting temperature of 110 ^{o}C. This poly(ester-alt-ether) copolymer can be useful materials not only for medical use, but also for general uses as films, molded products, laminates, foams, nonwoven materials, adhesives and coatings for temporary more universal uses. However, little attention has been paid to the synthesis and properties of PPDX. The main reasons are that its monomer, 1,4-dioxan-2-one, was not commercially available in the past, but also the low ceiling temperature of PPDX (265 ^{o}C) favors the unzipping depolymerization reactions in the molten state. Hence, the recent improvements in terms of activity and productivity will be discussed according to the key-parameters governing the synthesis and melt-processing of PPDX. Besides, the properties and applications of PPDX are given.
Key words: biodegradable polymers, copolymers, branched polyesters, controlled polymerization, 1,4-dioxan-2-one, poly(1,4-dioxan-2-one), polymer processing, thermodynamics of polymerization.

POSTĘP W SYNTEZIE I ZASTOSOWANIACH KOPOLIMERÓW NA PODSTAWIE POLI(1,4-DI-OKSAN-2-ON)U

Streszczenie — W niniejszej pracy przeglądowej, obejmującej 109 odnośników literaturowych, przedyskutowano najnowsze osiągnięcia w zakresie syntezy, właściwości i zastosowań poli(1,4-dioksan-2--on)u (PPDX, od ang. *poly*(*para-dioxan-2-one*). Szczególną uwagę poświęcono doborowi warunków procesu umożliwiających kontrolowaną syntezę i przetwarzanie PPDX w stanie stopionym. PPDX jest kolejnym, nowym materiałem wielkocząsteczkowym zdolnym do biodegradacji. Szczególnie interesujące są właściwości termomechaniczne PPDX, jak na przykład stosunkowo niska temperatura topnienia równa 110 ^{o}C. Z punktu widzenia struktury jednostki powtarzalnej, PPDX jest przemiennym kopolimerem estru z eterem. Oprócz specjalistycznych zastosowań w obszarze biomedycznym PPDX jest również szeroko wykorzystywany w postaci cienkich warstw (folii), produktów formowanych, laminatów, pianek, włóknin, klejów i powłok. Mimo szerokiego zakresu zastosowań mało uwagi

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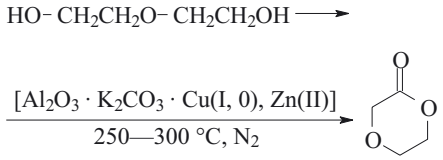
poświęcano dotychczas systematycznym badaniom dogodnych warunków syntezy i właściwości PPDX. Wynikało to z faktu, iż do niedawna monomeryczny 1,4-dioksan-2-on (PDX) nie był produktem handlowym oraz ze względu na depolimeryzację PPDX w stanie stopionym (górna graniczna temperatura polimeryzacji PDX wynosi T_c = 265 °C).
Słowa kluczowe: polimery biodegradowane, kopolimery, poliestry rozgałęzione, polimeryzacja kontrolowana, 1,4-dioksan-2-on, poli(1,4-dioksan-2-on), przetwórstwo polimerów, termodynamika polimeryzacji.

In recent decades, biodegradable polymers have attracted a lot of attention in biomedical realm as well as in daily applications [1—10]. In surgery, their functions are bonding (monofilament sutures, screws), closure (covering and occlusion), scaffold (cellular proliferation and tissue guide), separation (isolation and contact inhibition) and drug delivery devices [11, 12]. They offer the advantage of being biocompatible and bioresorbable, *e.g.* degrading in low molecular weight products, which are either excreted or metabolized. Besides, biodegradable polymers have also shown to be valuable substitutes for commodity polymers such as polyethylene (PE) and polypropylene (PP) in short-time applications like packaging [13].

Depending on their origin, biodegradable polymers may be classified into three categories: natural, naturally modified and synthetic polymers [14, 15]. Natural polymers offer the advantage of being available from renewable resources, and therefore attractive for the sustainable development [16]. However, due to the physicochemical limitations of natural polymeric materials, it is necessary to improve their properties either by melt blending with reinforcing compounds or by chemical modification [17]. Compared to natural biodegradable biopolymers, *e.g.* starch, and their modified derivatives, synthetic biodegradable polymers appear highly attractive owing to the versatility of tuning up their properties in function of molecular parameters and composition. Among them, aliphatic polyesters such as poly(ε-caprolactone) (PCL) and polylactides (PLA) have drawn a lot of interest from both the academic and industrial media [18, 19]. Indeed, these aliphatic polyesters exhibit mechanical properties comparable to PE and PP, while high molecular weight PCL and PLA can be readily produced by ring-opening polymerization (ROP) of their respective cyclic esters. ROP represents the most useful method for the synthesis of aliphatic polyesters with high molecular weights and low polydispersities, and allows the preparation of elaborated macromolecular architectures such as block copolymers. Interestingly enough, poly(1,4-dioxan-2-one) (PPDX) also obtained by ROP of 1,4-dioxan-2-one (PDX) appears to be another attractive candidate as a biodegradable substitute for commodity polymers [20]. This aliphatic poly(ester-alt-ether) copolymer offers a good compromise between its processing temperature and the service temperature range with a melting temperature (T_m) and glass transition temperatures (T_g) of 110 °C and –10 °C, respectively.

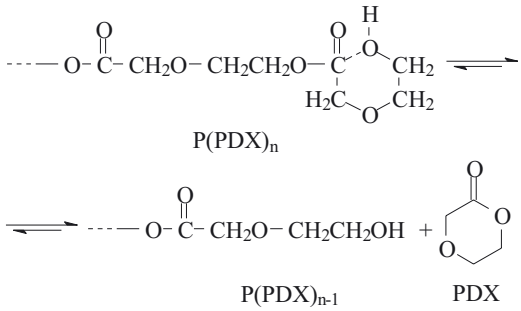
Albeit PPDX has interesting physical characteristics, and compared to the other widely studied polyesters such as PCL and PLA, only limited works have been done on the synthesis and properties of PPDX [21, 22].



(1)

The main reason was ascribed to the non-commercial availability of PDX monomer in the past, until its convenient one-step elaboration synthesis starting from an inexpensive substrate as disclosed in 1992 by Shell process for the preparation of PDX monomer by catalytic dehydrogenation of diethylene glycol using a copper(I)-based catalyst supported on silica particles [23].

Another long-term issue that has restricted the use of PPDX as bulk materials was connected with the low ceiling temperature of PPDX (265 °C), favoring unzipping depolymerization reactions in the molten state.



(2)

Consequently, the syntheses as well as the subsequent melt-processing of PPDX are characterized by the presence of relatively high amounts of residual PDX monomer in equilibrium with the PPDX chains [21—24]. In addition, similarly to most aliphatic polyesters, the choice of the initiating/catalytic system to promote the synthesis of PDX is of prime importance since it defines the mechanistic and kinetic parameters, and thus predetermines, at least partially, the production and processing conditions as well as the ultimate properties of PPDX [25].

In this respect, over the last ten years, a better understanding has been provided on the mechanistic, kinetic and thermodynamic factors that govern the polymerization and melt-processing of PPDX, and spectacular improvements have thereby been achieved in terms of activity and productivity [26]. Hence, this contribution

aims at focusing on the recent achievement and concerns about the synthesis, properties and applications of PPDX. Beyond kinetic, mechanistic and thermodynamic studies, different strategies enhancing the properties of PPDX in view of its thermal and hydrolytic stability will be discussed as well.

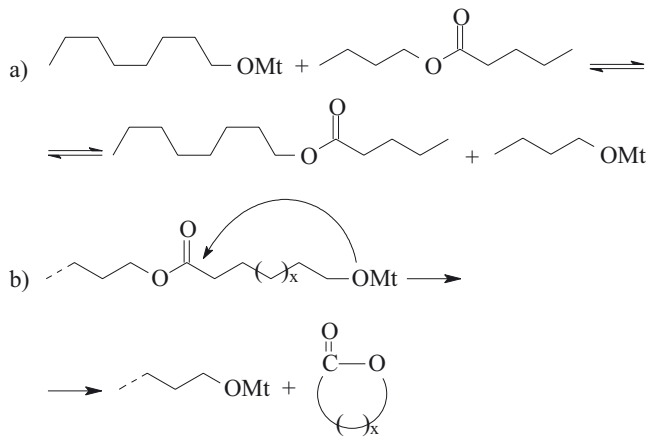
RING-OPENING POLYMERIZATION OF PDX

High molecular weight aliphatic polyester polymers with narrow molecular weight distributions can be readily obtained under relatively mild conditions by ROP of cyclic esters. Except for γ-lactones and a few substituted ε-lactones, ROP of lactones is thermodynamically favorable, *i.e.* when the free Gibb's enthalpy (ΔG_p) of this process is negative [23, 24, 27—29].

$$\Delta G_p = \Delta H_p - T\Delta S_p \quad (3)$$

The polymerization of four-, six-, and seven-membered cyclic esters is driven by the negative change of enthalpy due to their ring-strain ($\Delta H_p^0 < 0$; $\Delta S_p^0 < 0$, and $|\Delta H_p^0| > -T\,\Delta S_p^0$), whereas the driving forces in the larger ring (di)lactones results from a positive change of entropy ($\Delta H_p^0 \geq 0$; $\Delta S_p^0 > 0$, and $\Delta H_p^0 < |-T\,\Delta S_p^0|$). The presence of bulky substituents on the (di)lactone might further decrease the ring-strain of cycle.

The first attempts on ROP have mainly been carried out through anionic and cationic processes. However, in most cases, the resulting polyesters exhibited low molecular weight, and no control was reported due to the occurrence of intra- and intermolecular transesterification reactions, yielding a heterogeneous mixture of linear and cyclic oligomers (Scheme A) [30—33].



Scheme A. Inter- (a) and intramolecular (b) chain transfer reactions (where M_t = metal ion (according to [30—33])

Several authors have shown that the extent of these side reactions depends on the reactivity-selectivity principle. Using covalent metal alkoxides or carboxylates as (co)initiators represents an adequate way, at least, to suppress the occurrence of transesterification reactions, leading to polyesters having narrow molecular weight distribution. Some authors called those as pseudo-ionic ROP or coordinative ROP, involving coordination of cyclic esters with the covalent metal alkoxides or carboxylates through their vacant d orbitals. Accordingly, covalent multivalent metal alkoxides or carboxylates as (co)initiators [where metal is Al, Sn(II), Sn(IV), etc.] have enabled to achieve the best control in polymerization of PDX [32]. Within this review, a special attention will be paid to these frequently used catalyst/initiators in ROP of PDX in view of thermodynamic, kinetic and mechanistic considerations. Moreover, the enzymatic copolymerization of PDX as well as its thermally promoted ROP will be also discussed. To avoid the harmful effects of metallic residues in medically applied PPDX, enzymatic polymerization represents an eco-friendly process, using easily renewable resources as starting materials [34].

THERMODYNAMICS OF PDX RING-OPENING POLYMERIZATION

The first reports on PDX polymerization came from the early 1960s, but more systematic studies on the ROP have been started only recently [35]. Compared to other well-known polyesters, the major reason is due to the poor solubility of PPDX in the most current solvents such as toluene and acetone, which has discouraged the study ROP of PDX from the mechanistic and kinetic viewpoint. In this respect, first attempts to study the polymerization of PDX were carried out in absence of solvent (bulk conditions) [22]. In bulk, it has been observed that the polymerization of PDX leaves high amounts of unreacted monomer due to a quite low ceiling temperature. This can be described upon the microreversibility principle where all growing chains (P_n^*) are able to depolymerize until reaching a constant monomer (M) concentration [36, 37].

$$P_n^* + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} P_{n+1}^* \quad (4)$$

where: k_p, k_{dp} — *the propagation rate constant and the depolymerization rate constant, respectively*.

The equilibrium monomer concentration ($[M]_e$) can be adequately expressed by Dainton and Ivin's equation [36].

$$RT \ln[M]_e = \Delta H_p - T\Delta S_p^0 \quad (5)$$

where: ΔH_p — *the polymerization enthalpy under the experimental conditions*, ΔS_p^0 — *the entropy change at the standard state ($[M]_e$ = 1 mol · dm^{-3})*, R — *the gas constant*.

As studied in bulk ROP of PDX promoted by aluminum isopropoxide [$Al(O^iPr)_3$] at a temperature ranging from 60 to 150 °C, it has been observed that the equilibrium monomer concentration depends strongly on the final amorphous or crystalline state of PPDX, at least below its T_m value [38]. Figure 1 shows relation of $R\ln[M]_e$ versus $1/T$ for this polymerization with

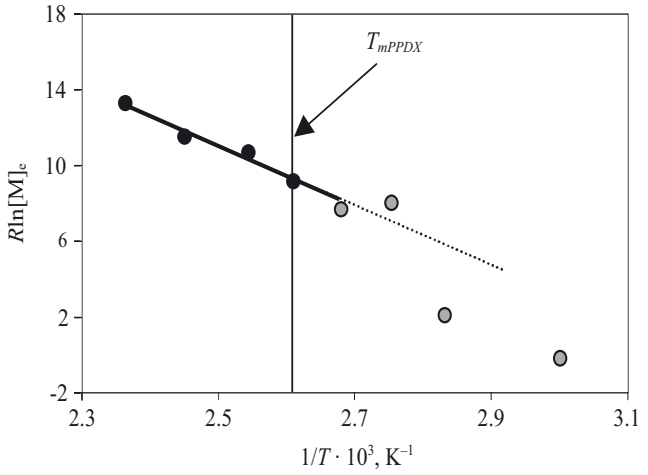


Fig. 1. Plot of $Rln[M]_e$ versus 1/T (K^{-1}) determined in bulk ROP of PDX initiated by $Al(O^iPr)_3$ (according to [38])

$[PDX]_0/[Al(O^iPr)_3]$ = 600 and reaction time of 14 h. Above *ca*. 110 °C, a linear regression analysis from relation presented determined an enthalpy of -15.8 kJ · mol^{-1} and a standard entropy of -50.4 J · mol^{-1} · K^{-1}.

These same values were obtained by calorimetric measurements of PPDX/PDX combustion (ΔH_p = -17 to -15 kJ · mol^{-1}) and in bulk polymerization of PDX promoted by different (co)initiating systems, *i.e.* tin octoate [$Sn(Oct)_2$] and triethylaluminum (ΔH_p = -14.1 kJ · mol^{-1} and ΔS_p^0 = -45.3 J · mol^{-1} · K^{-1}) [21, 39]. The last results indicated the independence of equilibrium monomer concentration whatever the nature of initiator. A ceiling temperature of 235 °C could be determined from eq. (5) upon the assumption that $[M]_e$ is equal to the initial monomer concentration, $[M]_0$. Below 110 °C, the reaction medium turned slowly hazy during the polymerization, indicating that PPDX was gradually crystallizing with increasing monomer conversion and reaction time. The crystallization of PPDX chains gradually leads to a reconcentration for both the residual monomer and the active aluminum alkoxides species within the amorphous regions, decreasing the relative $[M]_e$. Such a behaviour was reported in ROP of L,L-lactide carried out at temperatures lower than T_m value of the corresponding polyester [40]. Müller and coworkers [41] have even taken advantage of the crystallization of PPDX to extend the polymerization degree, upon a post-polymerization process treatment during the polymerization of PDX promoted with $Sn(Oct)_2$. In this method, the polymerization temperature was gradually reduced to temperatures lower than T_m of PPDX in order to maintain both polymerization rate and monomer conversion maximum as long as possible during the polymerization reaction. These optimal conditions were calculated based on the equilibrium polymerization kinetics, and compared with those obtained for polymerization reactions performed at constant temperature in the 80—180 °C range. Under these experimental conditions, reducing reaction temperature could optimize the polymerization process in order to achieve high conversions at lower temperatures and smaller reaction times. For instance, with their method, a 78 % conversion was achieved in a third of the time needed when carried out at a constant temperature of 80 °C. However, when the temperature of reaction medium was raised beyond T_m of PPDX, PPDX was prompted to depolymerize through unzipping depolymerization reactions, regenerating equilibrium PDX monomer again.

Furthermore cyclic PPDX oligomers has been observed in ROP of PDX promoted by $Sn(Oct)_2$/*n*-butanol both in bulk and in solution (in 1,4-dioxane). This has been shown using size exclusion chromatography (SEC) and matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry [42] as characterization tools. Increasing both temperature and monomer concentration in the feed increased the molar concentration of cyclic oligomers ($\Sigma i[CDX(i)]_{eq}$) up to maximum 1 mol · dm^{-3} for the polymerization of PDX. In addition, the solution ROP of PDX in 1,4-dioxane showed that the mass fraction (*f*) of cyclic oligomers after passing a maximum 40 % at $[PDX]_0$ = 4.0 mol · dm^{-3} at 100 °C decreased with increasing $[PDX]_0$, until reaching f < 10 % at 80 °C in bulk. It has also been observed by MALDI-TOF measurements that the dimer [CPDX(2)] was absent in the crude reacting mixture, probably because of its high ring strain. For the remaining cyclic PPDX oligomers, tetramer, pentamer, and hexamer exhibit a relatively large ring strain, being close to that of PDX monomer, which may result from transannular interactions. On the other hand, trimer, heptamer and octamer are almost strainless. In the latter case, their equilibrium concentration can be adequately predicted by the Jacobson-Stockmayer theory:

$$[CPDX(i)]_{eq} = A \cdot i^{-5/2} \quad (6)$$

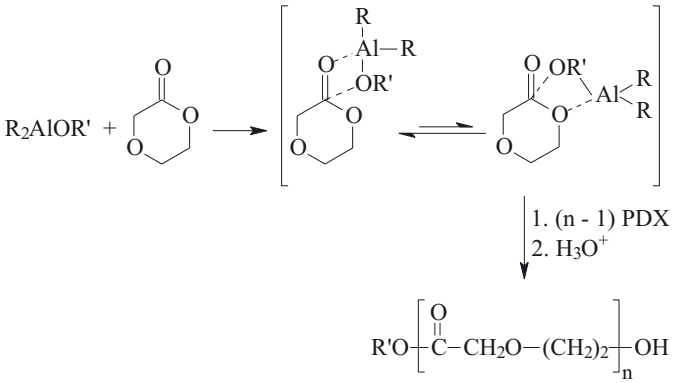
where: *i — the number of repeating units, and A = 1.87 mol · dm^{-3} corresponding to a constant characteristics for a given polymer chain*.

ALUMINUM ALKOXIDES AS INITIATING SYSTEMS FOR ROP OF PDX

Among initiating/catalytic systems, both aluminum mono- and trialkoxides have shown to be the most effective initiators to promote the ROP of various (di)lactones with high selectivity (restricted occurrence of termination and transfer reactions) allowing the preparation of high molecular weight polyesters and a huge range of novel macromolecular architectures both in solution and in bulk [43—47]. Interestingly enough, Kricheldorf *et al*. [22] first investigated the polymerization of PDX promoted by benzyl alcohol in the presence of zinc salts. Zn(II) lactate was selected as catalyst because of its easy handling and low toxicity for biomedical applications. However, even though long reaction times (several days) were required, some control over the molecular

weights of PPDX chains was attained by addition of benzyl alcohol as a (co)initiator at a fixed PDX/Zn salt ratio. Furthermore, by adding various bioactive alcohols or phenols, end-functionalized PPDX chains were made available.

Similarly but with a higher activity in terms of polymerization kinetics, aluminum alkoxide species have thus shown high efficiency in ROP of PDX. For instance, when $Al(O^iPr)_3$ was used as initiator, inherent viscosities for the resulting PPDX could be tuned up from the initial monomer/Al molar ratio [48]. The polymerization kinetics indicated first order in both monomer and initiator with an absolute rate constant of 0.08 $dm^3 \cdot mol^{-1} \cdot s^{-1}$ at 80 °C. This means that high molecular weight PPDX can be obtained within a few minutes while keeping a quite narrow polydispersity ($M_w/M_n < 1.3$) as shown by SEC. ROP of PDX proceeds through the well-known coordination-insertion mechanism that involves the coordination of the lactone onto the initiator, followed by the insertion of the monomer into the Al-O bond of the initiator through an O-acyl cleavage of the cyclic ester bond (Scheme B) [38].

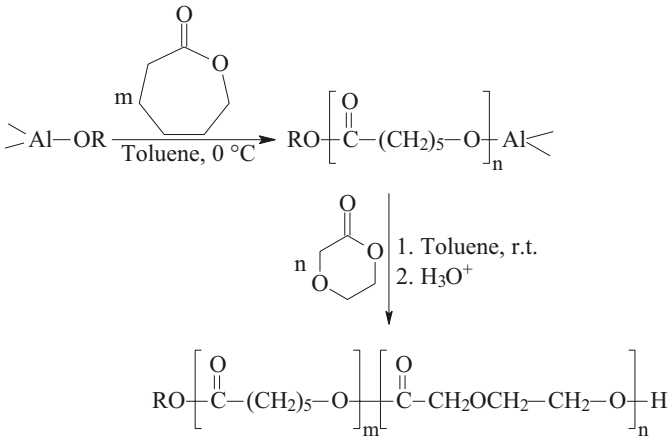


Scheme B. Coordination-insertion mechanism for ROP of PDX (according to [38])

Selective hydrolysis of the active aluminum alkoxide leads to the formation of a hydroxyl end-group, whereas the other extremity is capped by an ester function carrying the alkoxide radical from the initiator. Such a coordination interaction has been evidenced by ^{27}Al NMR and ^{13}C NMR spectroscopies using γ-butyrolactone (γ-BL) as a difficultly polymerizable lactone model of ε-caprolactone (CL) [49].

As an alternative pathway and in order to facilitate the characterization of PPDX chains by enhancing their solubility in conventional solvents such as toluene or tetrahydrofuran (THF), the PDX polymerization was performed with ω-aluminum alkoxide PCL chains as a macroinitiator that is highly soluble in toluene at 25 °C (Scheme C).

The PDX copolymerization proved to be living and well controlled, and led to novel poly(ε-caprolactone-*b*-



Scheme C. PDX copolymerization initiated by living ω-Al alkoxide PCL chains (with R = ^iPr) (according to [48])

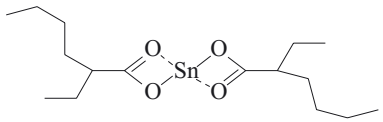
-1,4-dioxan-2-one) [P(CL-*b*-PDX)] block copolymers with controlled molecular weight and composition. Interestingly, proton nuclear magnetic resonance (^1H NMR), photocorrelation spectroscopy (PCS) and transmission electronic microscopy (TEM) measurements indicated the formation of colloids attributed to a growing PPDX core surrounded by a highly solvated PCL shell along the PDX polymerization in toluene [48]. This strategy had been previously applied to the ROP of glycolide promoted again by ω-aluminum alkoxide PCL macroinitiator in THF [poor solvent for the polyglycolide (PGA) sequence] with the formation of well-defined poly(ε-caprolactone-*b*-glycolide) with molecular weights as high as 70 000 for the PGA block [50].

According to the unique kinetic characteristic features provided by aluminum alkoxides, bulk copolymerization of PDX was carried out by initiation with aluminum sec-butanoxide [$Al(O^{sec}Bu)_3$] in a co-rotating twin-screw extruder through a fast single-step and continuous process [51, 52]. To limit the occurrence of unzipping depolymerization reactions during the synthesis and the processing of PPDX, PDX was copolymerized with low amounts of comonomer such as CL [53]. Both homopolymerization and copolymerization of PDX and CL proceeded very rapidly with comonomer conversions that were almost complete when 8 mol. % initially added in the feed. This indicated that the equilibrium monomer may interact either stronger or weaker with a foreign active center than with its own. Therefore, adding another comonomer in highly equilibrated polymerization systems such as ROP of PDX allows shifting the equilibrium polymerization to copolymer chains instead of comonomers with, therefore, the complete conversion of comonomers. Interestingly, semi-crystalline melt-stable PDX-based copolymers could be obtained through such a reactive extrusion process. Therefore this single-step and continuous reactive extrusion strategy has opened the door to a more cost-competitive PDX polymerization process leading to commercially viable

PPDX with respect to other existing biodegradable polymers.

TIN CARBOXYLATES AS INITIATING SYSTEMS FOR ROP OF PDX

As aforementioned, covalent metal carboxylates, particularly tin(II) octoate [$Sn(Oct)_2$], which molecular structure is presented by Formula (I), belong to the most frequently used catalysts for the polymerization of cyclic esters for industrial purposes [47, 54, 55]. Such commercial catalysts can be more readily handled (*i.e.* do not

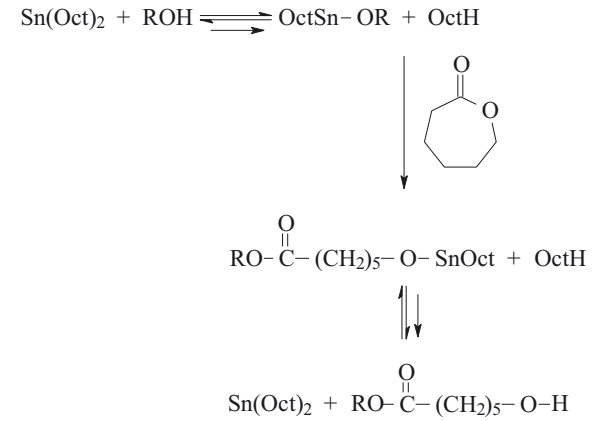


(I)

require high vacuum equipment) and are relatively easy to purify (at least down to *ca.* 2 mol. % of proton containing impurities) by distillation for semi-quantitative synthetic work. Furthermore, $Sn(Oct)_2$ has been approved as a food additive by Food and Drug Administration (FDA) [56].

The activation mechanism involves the in situ formation of Sn-alkoxide bonds located at the polymeric chain ends, proceeding through the so-called active chain end mechanism. Thus, through a rapid exchange equilibrium, $Sn(Oct)_2$ and most probably any other covalent metal carboxylates are first converted by reaction with protic compounds (ROH) into tin (or other metal) alkoxides as active centers for the polymerization [57—59]. The polymerization involves a coordination-insertion mechanism similarly to the previously discussed mechanism holding for covalent metal alkoxides (Scheme D).

However, even though a good control is achieved in ROP of PDX promoted by $Sn(Oct)_2$, a relatively longer reaction time is needed to obtain high molecular weight



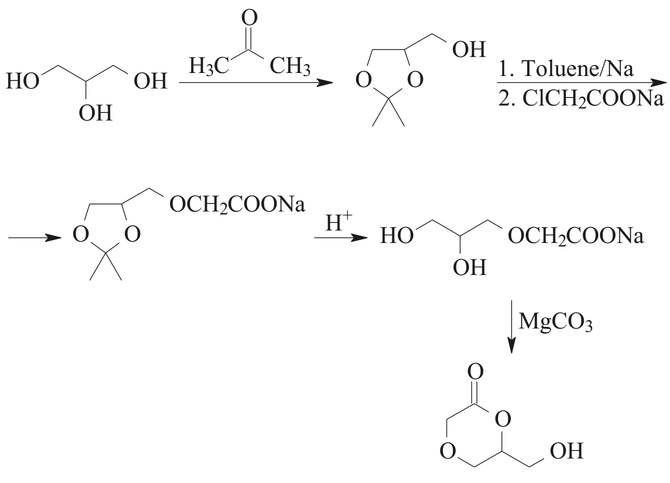
Scheme D. Activation mechanism for the catalyzed ROP of CL promoted by $Sn(Oct)_2$/ROH (only tri-monoalkoxide, Oct-Sn-OR is shown even though the formation of tin dialkoxide cannot be ruled out) (according to [57—59])

PPDX as compared to aluminum alkoxides. For instance, Nishida *et al.* [21] reported that PPDX with a number-average molecular weight of 80 000 was obtained in 20 h at 80 °C. In this respect, Li *et al.* [60] used microwave heating in order to boost the ROP of PDX promoted by $Sn(Oct)_2$ in a controlled way and under mild conditions. Microwave heating, which presents a totally different heating mode from conventional heating, has been proved to be more rapid and efficient in a wide variety of chemical reactions like polymerization. Addition polymerization [61, 62], condensation polymerization [63, 64], graft polymerization [65, 66], and ROP [67—69] has been studied, particularly for monomers like PDX containing polar groups readily able to absorb microwaves [70]. In this respect, rapid ROP of PDX was carried out at constant microwave powers from 90 to 360 W, respectively, in a microwave oven (frequency = 2.45 GHz) [60]. The resulting temperature for the polymerization medium ranged from 158 to 198 °C. For instance, when 10^{-4} mol. % of $Sn(Oct)_2$ was used as co-initiating system at 270 W, the polymerization yield for PPDX with a viscosity-average molecular weight (M_v) of 156 000 reached 63 % after 25 min in contrast to more than 14 h to obtain the same characteristic PPDX by conventional heating method at 180 °C. However, recent results have shown that $AlEt_3$ was even more effective for the microwave-irradiated PDX polymerization [71]. When $AlEt_3$ was used, polymerization yield reached almost 97 %, with a PPDX molecular weight close to 197 000, much higher than those obtained with $Sn(Oct)_2$ as the ROP catalyst.

Besides these kinetic considerations, $Sn(Oct)_2$ has shown to be also effective in the controlled ROP of PDX by opening a wide range of macromolecular architectures such as (semi)telechelic polymers, (di)macromonomers, graft, (multi)block, and hyperbranched copolyesters [72]. For instance, well-defined triblock PPDX-*b*-Y-*b*-PPDX copolymers were synthesized by $Sn(Oct)_2$-promoted ROP of PDX, where the nature of Y was α,ω–dihydroxy poly(ethylene glycol) (PEG) [73—75], polytetrahydrofuran [76], and poly(trimethylene carbonate-*co*-ε-caprolactone) random copolymers [77] as macroinitiators. Interestingly, in the case of using α,ω–dihydroxy PEG as macroinitiator, the composition and the length of PPDX block could be finely adjusted in order to modify the thermal behavior, the thermal stability and the water absorption of the resulting triblock copolymers. As far as drug delivery applications were concerned, these PPDX-*b*-PEG-*b*-PPDX copolymers exhibited an amphiphilic character, where the hydrophobic part derived from PPDX can be adjusted by copolymerization of PDX with other cyclic esters such as CL and lactide (LA). Random increase in CL fraction improved the flexibility and hydrophobicity for the resulting polyester block [78]. When LA was used as comonomer, the same authors showed that the resulting triblock copolymer, P(PDX-*co*-LA)-*b*-PEG-*b*-P(PDX-*co*-LA), en-

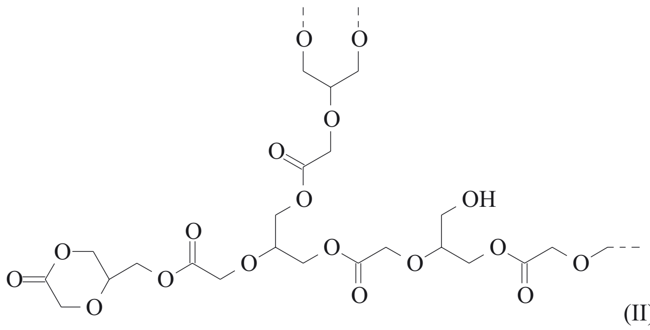
hanced the DNA transfection for the cationic lipid mediated DNA complexes into mammalian cells [79, 80].

Similarly, star-shaped PPDX was synthesized through ROP of PDX promoted by pentaerythritol/$Sn(Oct)_2$ in bulk [81]. Because of their particular architecture, such star-shaped polymers may have great potential in biomedical applications due to the higher polymer mass and functionality per unit volume compared to their linear analogous. However, the synthetic pathway was not well-controlled, leading to a mixture of two-armed and three-armed PPDX. The occurrence of variously armed star-shaped PPDX could be due to steric hindrance caused by adjacent growing chains, reducing the accessibility of PDX monomer to the unreacted hydroxyl groups from pentaerythiol. Recently, hyperbranched aliphatic polyester derived from functionalized PDX was selectively obtained by self-condensing ROP of 6-hydroxymethyl-1,4-dioxan-2-one (HDON). The unique attribute of such poly(6-hydroxymethyl-1,4-dioxan-2-one) (PHDON) is the exclusive presence of primary hydroxyl groups [82]. The reactivity of the primary OH groups enables higher branching degree of the resulting polyester. The OH groups, present in high quantity on the outer sphere of the macromolecules, can be further modified making the PHDON a promising material for drug delivery. A ring-closure route starting from glycerol was employed to obtain HDON slightly contaminated with 6-hydroxyl-1,4-dioxapan-2-one (Scheme E).



Scheme E. Synthesis of 6-HDON (according to [82])

Regarding the hyperbranched polyester, self-condensing ROP of HDON was carried out at 110 °C in the presence of $Sn(Oct)_2$ to afford the corresponding hyperbranched polyester. Relatively rapid reaction rate was achieved when the catalyst concentration was fixed at 4.10^{-2} mol. % of $Sn(Oct)_2$ for monomer conversions close to 98 % after 24 h. Once the maximum of the molecular weight was reached, prolonged reaction time led to a slight decrease in molecular weights. The $Sn(Oct)_2$ concentration proved of utmost importance in the molecular weight of PHDON. Molecular weights in polyester as high as 25 000 could be obtained for $Sn(Oct)_2$ concentrations higher than 10^{-2} mol. % and lower than $8 \cdot 10^{-2}$ mol. %. However, the polydispersities of all-obtained polyesters were comparatively broad, indicating characteristic of self-condensing polymerizations. In addition, the hyperbranched polymer contained both primary and secondary hydroxyl groups. A similar study was carried out using 5-hydroxyl-1,4-dioxapan-2-one (5-HDON) as a monomer [83]. This monomer was selectively recovered through a modified Brogini's procedure involving a thermal decomposition step. Interestingly, when polymerized under particular conditions (depending on the

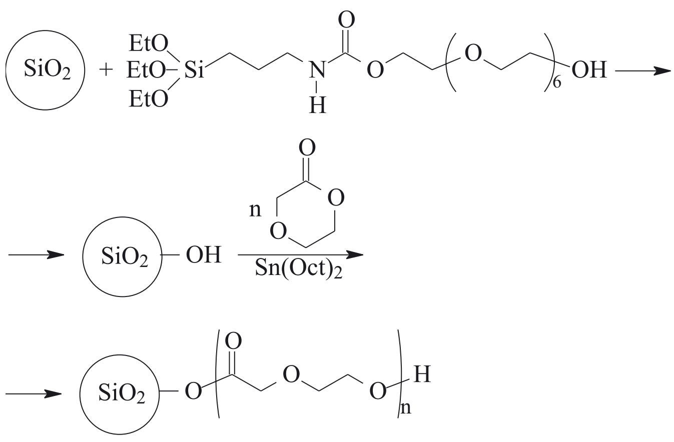


(II)

catalyst and the reaction conditions), the resulting polymer exhibited hyperbranched structures containing exclusively primary hydroxyl groups [Formula (II)].

The grafting-from method was utilized in the surface-initiated ROP of PDX promoted by $Sn(Oct)_2$ in toluene at 60 °C. In the first step, self-assembled monolayers were formed by adding hydroxyl-terminated triethyloxysilane to a solution of silica particles in xylene (Scheme F) [84]. It is worth noting that the ethylene-glycol-tethered was selected to generate relatively flexible, enabling to grow polymers in a controlled manner from these kinds of surface.

^{1}H NMR and FT-IR spectroscopies attested for the selective formation of PPDX chains attached to these silica particles. Upon polymerization, field emission scan-



Scheme F. General procedure for the synthesis of PPDX grafted onto silica particles (according to [84])

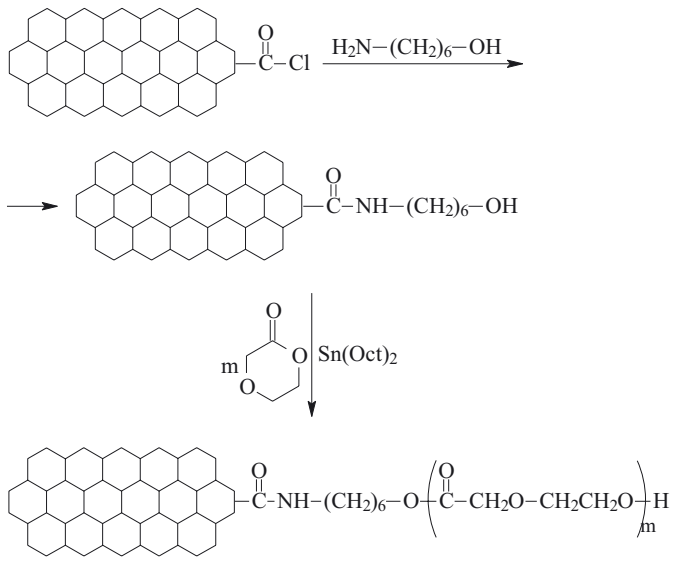
ning electron microscopy images show that the average particle diameters increased from 490 to 750 nm. In a similar way, the same authors carried out the surface-initiated ROP of PDX for forming PPDX-based nanocomposites containing single-walled carbon nanotubes (SWCNT) [85]. The synthetic pathway consisted of three simple steps:

— chemical preparation of shortened SWCNT (s-SWCNT),

— covalent attachment of the polymerization initiator,

— surface-initiated ROP of PDX in the presence of $Sn(Oct)_2$.

s-SWCNT were prepared by oxidation of pure SWCNT in a mixture of concentrated H_2SO_4 and HNO_3, followed by addition of H_2O_2. The generated carboxylic acid groups at the tips and other high defect density sites of s-SWCNT. The attachment of 6-amino-1-hexanol onto the resulting s-SWCNT was then carried out in order to form a valuable initiator for surface-initiated ROP of PDX (Scheme G). Thermogravimetric analysis (TGA) shows that the thermal stability for PPDX chains upon



Scheme G. Surface-initiated ROP of PDX onto s-SWCNT (according to [85])

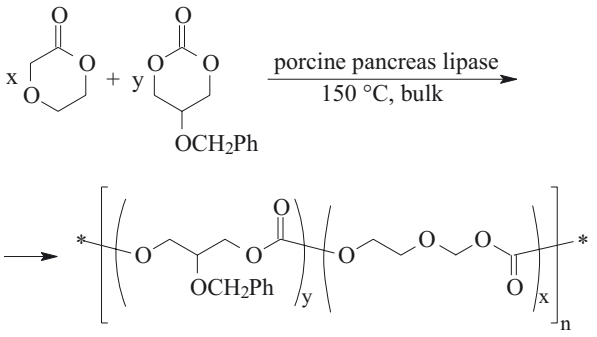
the formation of s-SWCNT/PPDX composites was much higher than neat PPDX. This indicated some beneficial interactions between PPDX chains and s-SWCNT.

Some experimental support was provided for the coordination-insertion mechanism involved in the surface-initiated ROP of PDX as promoted by $Sn(Oct)_2$ [86]. The "grafting-from" method was carried out through ROP of PDX initiated from a gold surface modified with 1-mercaptoundec-11-yl-tri(ethylene glycol) in toluene. The polymerization temperature was set at 55 °C, to avoid the thermal degradation of Au-S bond above 60 °C. After removing any physically absorbed PPDX upon thorough washing with 1,1,1,3,3,3-hexafluoro-2-propanol, X-ray photoelectron spectroscopy and secondary ion mass spectrometry revealed that tin species was attached to the polymer chain. This supports the coordination-insertion mechanism proposed by Duda and coworkers [57—59] that the actual initiating species are formed by the exchange between $Sn(Oct)_2$ and the hydroxyl groups. However, due to the lack of solubility for PPDX, the authors reported that the activated monomer mechanism might also occur through the formation of a complex between the Lewis acid [$Sn(Oct)_2$] and the carbonyl group of PDX monomer.

NON-METALLIC INITIATING SYSTEMS IN ROP OF PDX

Enzymes have emerged as powerful catalysts for the preparation and chemical recycling of green and sustainable polymers obtained by ROP [87]. Lipases as enzymes have shown to be promising in the polymerization of a great variety of lactones because they can preserve their activity in organic medium at high temperature [88]. In order to improve activity in ROP, immobilization of lipase is currently carried out on, *e.g.* celite. This leads to polyesters with higher molecular weight but also larger polydispersity indices. However, lipase-initiated ROP of macrolactones has proved advantageous when compared to more conventional metallic initiators/catalysts. When such conventional initiators/catalysts are used in contrast to enzymes, ROP of macrolactones proceeds slowly, but also yields low molecular weight polyesters. In lipase-initiated ROP, smaller-sized lactones such as PDX monomer have also be considered in order to avoid the harmful effect of metallic residues in medically applied aliphatic polyesters. Nishida *et al*. [34] studied different enzymes (lipases, esterase, and protease) in bulk ROP of PDX at 60 and 100 °C. This study revealed that immobilized lipase *candida antartica* exhibited very high catalytic activity. Only 0.5 wt. % of lipase was enough to show higher polymerization activity than 5 wt. % of other enzymes at 60 °C. High molecular weight PPDX with a multimodal molecular weight distribution could be prepared by ROP in presence of immobilized lipase *candida antartica*. The origin of the multimodal molecular weight distribution was explained by the heterogeneity of the polymerization system, together with the simultaneous degradation process through unzipping depolymerization reactions. A slight amount of water proved necessary by acting not only as a substrate for the initiation process, but also as a chain cleavage agent. However, excess water depressed the polymerization process. In general, water is involved in the initiation step through an enzyme-activated monomer mechanism proceeding *via* an acyl-enzyme intermediate at a serine residue of lipase. The key-step is the nucleophilic attack of the lactone by water, which is contained in the enzyme, yielding ω-hydroxycarboxylic acid as the propagation species [87, 88].

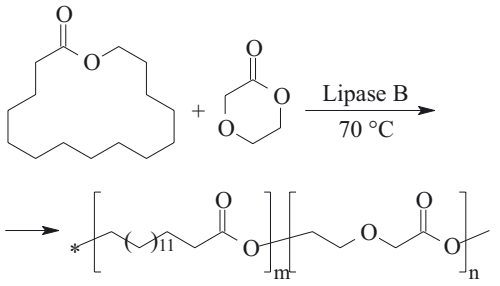
Enzymatic copolymerization of PDX with other cyclic monomers has also been investigated. For the first time, biodegradable copolymers were prepared by bulk copolymerization of PDX with 5-benzyloxy-trimethylene carbonate (BTMC) at 150 °C using immobilized *porcine pancreas lipase* (Scheme H) [89]. BTMC monomer was used to improve the solubility of PPDX, while introducing functional pendant groups for further modifications.



Scheme H. Enzymatic ring-opening copolymerization of BTMC with (according to [89])

Under the same conditions, no corresponding copolymers could be obtained in the absence of immobilized *porcine pancreas lipase*, indicating that the lipase enzymes play a catalytic role in the copolymerization of PDX with BTMC. When lipase enzymes are used, the BTMC monomer exhibited higher reactivity than PDX monomer, leading to random copolymers with higher BTMC contents than that in the feed. Interestingly enough, the copolymer compositions could be adjusted in such a way that the degradation rate of the resulting copolymers was well-tailored allowing the drug release of a model drug, *i.e.* ibuprofen, from being effective.

Recently Gross and its coworkers have prepared semi-crystalline random PDX-based copolymers by ring-opening copolymerization of PDX with ω-pentadecalactone (PDL) promoted by *candida antartica lipase B* in toluene at 80 °C (Scheme I) [90]. The resulting copolymer was of great interest because PDL repeating units have substantially lower hydrophilicity than PDX units, altering or reducing the PPDX biodegradation. ^{1}H NMR and ^{13}C NMR spectroscopies attested for the formation of a random copolymer with a slight tendency toward alternating arrangement. However, due to low ceiling temperature of PPDX, the yields for the resulting copolymers were typically in the 50—90 wt. % range.



Scheme I. Copolymerization of PDL with PDX promoted by candida antartica lipase B (N435) in toluene at 70 °C (according to [90])

Well-defined α,ω-dihydroxy telechelics PPDX oligomers ($1800 < M_n < 4200$) have been also synthesized through a non-catalyzed ROP of PDX in the presence of ethylene glycol as bifunctional initiator [91]. The synthetic pathway arises from the use of PPDX oligomers that are soluble enough at room temperature in chlorinated solvents for the preparation of multiblocks through chain extension reactions. For the sake of comparison, the polymerization was performed in bulk at 110 °C without or with dibutyltin oxide as catalyst, but also in the presence of ethanol as a monofunctional initiator model.

The polymerization performed with dibutyltin oxide reached the polymerization/depolymerization equilibrium after 7 h reaction time, while a 48 h reaction time was necessary for the non-catalyzed ROP of PDX. With or without catalyst, kinetic measurements showed that there was no remarkable difference in apparent kinetic constant [$k_{app}(I^*)$] between the two different initiators with respect to the functionality of the alcohol. This indicates that hydroxyl groups from ethylene glycol were completely active in the thermally-activated polymerization of PDX. A nearly linear relationship for the M_n of PPDX oligomers versus PDX conversion was obtained; together with low polydispersity indices. In addition, the telechelic structure of resulting oligomers was evidenced by MALDI-TOF measurements. In contrast, with dibutyltin oxide, some discrepancy between M_{nPPDX} and PDX conversion was observed due to the presence of cyclic PPDX oligomers generated through unzipping depolymerization reactions in the crude reaction medium. This indicates that the non-catalyzed ROP of PDX can represent a promising thermal transesterification reaction in order to prepare well-defined oligoPPDX diols. Interestingly, the resulting telechelic polyesters proved semicrystalline with T_m value between 86 and 95 °C, which increases with PPDX molecular weight. As an example, the suitability of oligoPPDX diols as prepolymers for the synthesis of multiblock copolymers was demonstrated by polyaddition reactions between oligoPPDX, oligopoly(rac-lactide) diols and 2,4,4-trimethylhexane diisocyanate. The resulting copolyesterurethanes exhibited good elastic properties, but also a thermally-induced shape memory effect with a switching temperature between room temperature and body temperature, which would be of interest for smart biodegradable sutures.

PROPERTIES OF PPDX

PPDX is a biodegradable and biocompatible semicrystalline poly(ester-alt-ether), which is thus charac-

terized by a T_g at *ca*. -10 °C and T_m around 110 °C. PPDX has shown to be tougher than polylactides and even PE-HD with a tensile strength close to 50 MPa for an ultimate elongation ranging from 500 to 600 % [23]. Clearly and compared to the other widely studied polyesters, the major drawback of PPDX is its poor solubility in the most commonly used solvents such as toluene, acetone and tetrahydrofuran, which has discouraged many from studying the PPDX synthesis from the viewpoint of mechanistic approach and tentative control. Good solvents for high molecular weight PPDX are rather exotic solvents like hexafluoroisopropyl, 1,1,2,2--tetrachloroethane and 1,2-dichloroethane, which furthermore require refluxing for allowing the PPDX solubilization. To be complete, note that low molecular weight PPDX chains are soluble in chlorinated solvents as simple as chloroform and dichloromethane. PPDX is also soluble in solvents like dimethylsulfoxide and *N*,*N*--dimethylformaldehyde at room temperature, but its sensitivity to hydrolysis becomes a major drawback [26].

The melt-stability of PPDX is also an important property affecting the proper choice of processing and application temperatures. Due to its low ceiling temperature, severe thermal degradation occurs during the thermal processing of PPDX such as melt-molding and spinning [53]. As an example, Kricheldorf and Damrau [22] found that the thermal degradation of PPDX began at *ca*. 200 °C, and reached almost quantitative decomposition at 320 °C. It has been reported that the thermal decomposition of PPDX under inert atmosphere proceeds through a zero-order unzipping depolymerization, and to some extent at the early stage *via* ester pyrolysis degradation [92, 93]. The activation energies of these thermal degradations can be also enhanced under oxidative atmosphere such as air [94]. In order to improve its thermal properties, trichloroacetyl isocyanate, pyromellitic anhydride, methylcyclohexene-1,2-dicarboxylic anhydride, 4-methylcyclohexane-1,2-dicarboxylic anhydride were employed as end-capping reagents to react with the hydroxyl end-groups of PPDX chains [53, 92, 95]. End-capping enables to suppress the main chain scission under heating conditions in the melt-stability. The smaller the end-capping group or block, the lower the reduction of the degradation rate. Such a behavior might reflect the probability of having some chain scissions within the PPDX block making free new ω-hydroxyl end-groups from which unzipping could proceed. In other words, the best way to prevent or at least limit the PPDX degradation by unzipping, while keeping its intrinsic thermal properties, should be to randomly distribute a limited amount of CL or δ-valerdactone units all along the PPDX backbone. With this respect, it has been proposed to simultaneously copolymerize PDX and CL in bulk with PDX-rich starting feed compositions through one-step reactive extrusion processing [51]. Interestingly, it results that the thermal stability of PPDX chains is substantially improved by copolymerizing PDX with limited amounts of CL. Differential scanning calorimetry (DSC) analyses of the as-prepared P(PDX-*co*-CL) copolymers show that a CL molar fraction as high as 11 mol. % does not prevent the crystallization of the resulting copolymer, which retains T_m value close to 95 °C. The formation of a blocky-like copolymer structure can explain this, in which short PPDX and PCL sequences are randomly distributed.

As aforementioned, Gross and coworkers prepared semicrystalline random P(PDX-*co*-PDL) copolymers by enzymatic ring-opening copolymerization of PDX [90]. Although both ^{1}H NMR and ^{13}C NMR spectroscopies attest for the formation of a random copolymer with a slight tendency toward alternating arrangement, crystallization and melting phenomena for the resulting copolymers could be observed independent of the composition in comonomer. In general, random copolymers are expected to show a progressive decrease in crystallinity with increasing comonomer content and degree of randomness, unless the repeat units undergo isomorphous substitution. In contrast, wide-angle X-ray scattering and DSC measurements show that PDX units can crystallize in the poly(ω-pentadecalactone) lattice as isodimorphism of the random copolymers, explaining the high crystalline content of all copolymers with PDX content ≤ 57 mol. %. In addition, while being semicrystalline, copolymerization of PDX with PDL was found to remarkably enhance PPDX thermal stability at PDX content higher than 30 mol. %.

Some additives such as 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMP) were used as catalyst deactivators when PPDX contains some residual catalyst [96]. It is well known that BMP is an excellent chelator to a majority of metal ions, and has been applied extensively in analytical chemistry and radiochemistry. Indeed, beside their ability to promote ROP of PDX, the residual catalyst can also catalyze intra- and intermolecular transesterification reactions, accelerating the thermal decomposition of PPDX. For sake of comparison, when BMP was added, the thermal stability of PPDX was improved under oxidative atmosphere (air) by the formation of stable chelate complexes as compared to as-prepared PPDX and PPDX purified by precipitation.

In order to improve the melt-stability of PPDX, Huang *et al*. [97] have prepared PPDX/montmorillonite (MMT) through *in situ* ROP of PDX promoted by triethylaluminum in bulk at 50 °C. Polymer-layered silicate nanocomposites represent a new class of organic-inorganic materials that have shown unexpected properties such as large increase in the thermal stability, mechanical strength, and impermeability to gases such as water and oxygen at low content in layered silicate nanoplatelets (< 5 wt. %). However, the dispersion state of the clay layers within the polymer matrix (intercalation and exfoliation) is utmost importance for the final properties of the resulting nanocomposites that are relied onto the synthetic pathway, the nature of the clay,

and clay concentration. Three montmorillonite, *i.e.* commercial Cloisite clays (natural Cloisite Na^+, Cloisite-1831 as modified by octadecyltrimethyl ammonium chloride, and Cloisite-OH as modified by hydroxyethylhexadecyldimethyl ammonium bromine) are used in this work. As a result, intercalated structures could be obtained, leading to improve thermal stability for the resulting PPDX nanocomposites. Both T_g and T_m values increase upon the addition of clay nanoplatelets, due to a nucleating effect provided by the nanoclays.

BIODEGRADATION OF PPDX

PPDX is a biodegradable and biocompatible poly(ester-alt-ether) copolymer. The ether bond endows flexibility and hydrophilicity to PPDX, but also causes marked hydrolysis [98]. Sabino *et al*. [99, 100] determined the hydrolytic degradation process of PPDX either in distilled water or a phosphate buffer (pH = 7.44) at 37 °C. When the buffer phosphate is used as a hydrolysis medium, the changes in pH as degradation proceeds decreased with time. This indicated that hydrolysis is producing low molecular weight PPDX that have acidic character and are water-soluble as one can except from hydrolysis of ester linkages. These acid species can also participate as catalyst during the hydrolysis of PPDX. This increase in pH also indicated that the buffer capacity has clearly been exceeded during the study. When distilled water is used as hydrolysis medium, there is no buffer to balance the pH, and the acidity of the medium is higher, accelerating the hydrolysis of PPDX chains. The evolution of the viscosity average molecular weight against time shows that the hydrolytic degradation of PPDX proceeds in an approximate two-stage process. Initially, water diffuses faster to the less dense amorphous regions, and hydrolyzes the ester functions of PPDX chains as compared to the compact crystalline regions. Although both regions are being attacked at the early stage of the experiment, the attack rate of the amorphous region is faster. The overlap of these two types of kinetics against time generates an apparent two-stage process. Such results support the theoretical model proposed by Nishida *et al*. [101] that predicts the change in PPDX molecular weight during the autocatalytic random hydrolysis.

The hydrolytic degradation of PPDX however depends on the molecular weight, the molecular structure (*e.g.*, random copolymer), the shape, the orientation of the material, and the presence of additives [102—106]. Other authors have modulated the hydrolytic degradation of PPDX by adding a poly(vinyl alcohol)-*g*-PPDX graft copolymer [107]. This latter was obtained by bulk ROP of PDX promoted through partially protected hydroxyl poly(vinyl alcohol) in the presence of $Sn(Oct)_2$. Increasing the copolymer content enhances the degradation rate of resulting melt-blends, indicating that the degradation rate can adjusted upon the number and length of PPDX segments within the poly(vinyl alcohol)-*g*-PPDX graft copolymer.

Copolymerization of PDX with other cyclic monomers has shown to be another way to modify the hydrolytic degradation of PPDX. For instance, random P(BTMC-*co*-PDX) copolymers obtained by enzymatic degradation degrade much slower as PPDX can do. The reason was that BTMC is more hydrophobic than PDX, reducing the water diffusion into polymeric matrix and therefore reducing the relative degradation rate [89].

Microbial degradation of PPDX was first revealed by Nishida *et al*. [108, 109]. Many kinds of microorganisms are available to degrade PPDX in natural environments, similarly to poly(alkanoate)s such as poly(hydroxybutyrate) and PCL. From NMR and high pressure liquid chromatography measurements, the resulting products mainly contained monomeric acid. There are due to the degradation of PPDX into soluble oligomeric acids like in PLLA decomposition, and did not substantially utilize them.

Finally, *in vitro* biocompatibility of PPDX was assessed by studying cell adhesion and cell growth of fibroblastic cells on the polymer film themselves as in media enriched with the hydrolytic degradation products of PPDX [110]. It resulted that PPDX fulfills the criteria of bioadsorbability, namely good levels of cell adhesion and cell growth. In addition, the products as generated by hydrolytic degradation of PPDX did not provide any cytotoxicity, representing a crucial parameter in view of using degradable polymers such as PPDX for biomedical applications.

APPLICATIONS OF PPDX

With outstanding biodegradability and bioadsorbability, PPDX represents a candidate not only for medical use, but also for general uses as films, molded products, laminates, foams, nonwoven materials, adhesives and coatings for more universal temporary uses [98]. PPDX was the first clinically tested synthetic monofilament sutures manufactured by Ethicon, Inc. under the trade name PDS®. The presence of an ether bond endows great flexibility and hydrophilicity to PDS® suture with good tenacity and knotting behavior compared to traditional sutures based on glycolide/lactide such as VICRYL®, DEXON® and POLYSORB®. Furthermore, the monofilament loses 50 % of its initial breaking strength after 3 weeks of *in vivo* biomedical testing, and is totally absorbed within 6 months, providing an advantage over DEXON® or other products for slow-healing wound [102]. Copolymers of PDX with glycolide or trimethylene carbonate have also been reported for the preparation of sutures with improved properties as well as for the preparation of drug delivery systems [111]. Recently, potential shape-memory polymers obtained by coupling reactions between oligoPPDX and oligoPCL diols have been developed as smart degradable sutures. This

enables bulky implants to be placed in the body through small incisions that are able to perform complex mechanical deformations automatically [112]. OligoPCL diols were chosen as the precursor for the switching segment having T_m value close to body temperature (37 °C). OligoPPDX diols were chosen as the hard segment to provide the physical crosslinks with a higher T_m as adjustable with the length of oligoPPDX diols. These two macrodiols were then coupled with 2,2(4),4-trimethylhexanediisocyanate, leading to multiblocky copolymers with shape-memory properties adjustable on the composition of both macrodiols.

CONCLUSIONS AND OUTLOOK

PPDX represents a promising candidate as a biodegradable substitute, because of its interesting thermomechanical properties such as T_m value of 110 °C. The most useful method for the synthesis of high molecular weight PPDX relies upon ROP of PDX. However, due to its low ceiling temperature, the syntheses as well as the subsequent melt processing of PPDX are characterized by the presence of relatively high amount of residual PDX monomer in equilibrium with the PPDX chains. Like most aliphatic polyesters, the choice of the initiating/catalytic system to promote the synthesis of PPDX is of prime importance since it defines the mechanistic and kinetic parameters, and thus predetermines, at least partially, the production and processing conditions as well as the ultimate properties of PPDX. Aluminum alkoxides represent certainly belong to the best initiating systems for the controlled ROP of PDX in terms of molecular parameters, opening the way to a wide range of molecular structures and topologies. Besides these fundamental considerations, it is highly desirable to improve the thermal stability of PPDX through end-functionalization of hydroxyl-terminated PPDX chains or through copolymerization of PDX with other (di)lactones. The best way to prevent or at least limit the PPDX degradation by unzipping, while preserving its intrinsic thermal properties, has been to distribute a limited amount of comonomers such as CL all along the PPDX backbone randomly. Moreover, these thermostable and semicrystalline P(PDX-*co*-CL) copolymers can be produced within very high yield (low content of residual monomer) through a continuous and fast reactive extrusion process enhancing the cost-competitiveness and commercial viability with respect to commodity polymers.

With outstanding biodegradability and bioadsorbability, PPDX can be a promising candidate not only for medical use, but also for general uses as films, molded products, laminates, foams, nonwoven materials, adhesives and coatings for more universal temporary uses. Moreover, the use of non-organometallic promoter such as *N*-heterocyclic carbenes shall represent an interesting way for the controlled ROP of PDX, while avoiding the harmful effects of metallic residues in medically applied PPDX-based materials. Indeed, these simple organic molecules as catalysts or promoters in polymer synthesis have proved to provide elegant organocatalytic alternatives to traditional organometallic reagents [113].

ACKNOWLEDGMENTS

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— *G. Janowska, W. M. Rzymski, M. Kmiotek, A. Kucharska, A. Kasiczak* — Właściwości termiczne i palność chlorosulfonowanego polietylenu

— *V. Sáenz de J. Arbona, A. Ribes-Greus* — Wpływ fotooksydacyjnego starzenia w warunkach naturalnych na dynamiczne właściwości mechaniczne mieszanin PE-LD/PE-LLD (*j. ang.*)

— *M. Łapkowski, S. Golba, J. Żak, A. Stolarczyk, J. Sołoducho, J. Doskocz, W. W. Sułkowski, M. Bartoszek* — Polimery przewodzące zawierające jednostkę fenotiazynową w łańcuchu głównym

— *B. Vasheghani F., F. H. Rajabi, M. H. Ahmadi, A. Gholehzadeh* — Wpływ siły jonowej roztworu niektórych kompleksów interpolimerowych z udziałem wiązań wodorowych na stabilność i parametry termodynamiczne takich układów (*j. ang.*)

— *I. Kaya, S. Çulhaoglu* — Otrzymywanie, struktura i właściwości nowych oligo(eterów azometinowych) zawierających lub nie atomy chloru w łańcuchu głównym (*j. ang.*)

— *P. Rybiński, G. Janowska* — Wpływ budowy sieci przestrzennej kauczuków nitrylowych na ich właściwości termiczne

— *Czech* — Inicjatory rodnikowe i ich wpływ na lepkość i ciężar cząsteczkowy polimerów poliakrylanowych stosowanych w rozpuszczalnikowych klejach samoprzylepnych

— *R. Steller* — Przepływ uogólnionych cieczy newtonowskich w kanale ślimaka układu uplastyczniającego wytłaczarki