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Articles

Some Thermodynamic, Kinetic, and Mechanistic Aspects of the Ring-Opening Polymerization of 1,4-Dioxan-2-one Initiated by $Al(O^iPr)_3$ in Bulk

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ABSTRACT: 1,4-Dioxan-2-one (PDX) was polymerized in bulk by means of aluminum triisopropoxide ($Al(O^iPr)_3$) as initiator. Thermodynamic parameters and ceiling temperature were determined from the temperature dependence of the monomer conversion over the range from 60 to 150 °C. It highlights that the thermodynamic equilibrium monomer conversion depends strongly on the final amorphous or crystalline state of poly(1,4-dioxan-2-one) (PPDX), at least below its melting temperature. The kinetics of the PDX polymerization for various monomer-to-$Al(O^iPr)_3$ ratios at 80 °C is typically first order in both monomer and initiator and characterized by an absolute rate constant of 0.08 L mol^{-1} s^{-1}. Molecular weight increases regularly with monomer conversion and initial monomer-to-Al ratio, while polydispersity is kept quite narrow all along the polymerization ($M_w/M_n < 1.3$). Mechanistic investigations proved that $Al(O^iPr)_3$ is an efficient initiator for promoting the ring-opening polymerization that proceeds through a coordination−insertion mechanism with a selective rupture of the acyl−oxygen bond of the monomer.

Introduction

Poly(1,4-dioxan-2-one) (PPDX) is a biodegradable and biocompatible poly(ester-*alt*-ether). It totally degrades in the body within a period of 180 days.[1] PPDX has shown to be tougher than polylactides and even HDPE with a tensile strength close to 7000 psi for an ultimate elongation ranging from 500 to 600%.[2] With this respect, PPDX can be complementary to other biodegradable aliphatic polyesters by enlarging the available range of physical properties. It has been used to prepare monofilament sutures with good tenacity and knotting. Copolymers of 1,4-dioxan-2-one (PDX) with glycolide or trimethylenecarbonate have also been reported for the preparation of sutures with improved properties as well as for the preparation of drug delivery systems.[3−5] Thanks to its biocompatibility and performant physical properties, PPDX has attracted much attention as biomaterials for medical purposes, but it can also be useful as films, molded products, laminates, foams, nonwoven materials, adhesives, and coatings for temporary more universal uses.[6,7]

PPDX is thus an aliphatic poly(ester-*alt*-ether) which can be obtained by ring-opening polymerization (ROP) of 1,4-dioxan-2-one (PDX). The polymerization is usually promoted by organometallics such as tin(II) bis(2-ethylhexanoic acid) ($Sn(Oct)_2$),[8,9] triethylaluminum,[10] and derivatives of Ti, Zr,[11] and Hg.[10] To avoid harmful effects of metallic residues in medically applied materials, some nontoxic catalysts have also been investigated, including diethylzinc,[2,10] Zn lactate,[12] and very recently enzymatic catalysis.[13]

Recently, we reported on the efficiency of the ROP of PDX as initiated by aluminum alkoxide either in bulk or in solution.[14] Compared to $Sn(Oct)_2$, the use of $Al(O^iPr)_3$ as initiator for the bulk polymerization of PDX at 100 °C has allowed to tune up the inherent viscosity of the corresponding poly(ester-*alt*-ether) from the initial monomer-to-metal molar ratio. It has also enhanced the polymerization rate while decreasing the rate of the degradation through transfer reactions such as backbiting. Furthermore, regardless of the poor solubility of PPDX in common organic solvents, the PDX polymerization has been shown to be homogeneous and well controlled when initiated by ω-Al alkoxide PCL chains in toluene at room temperature.

This paper aims at reporting on the ring-opening polymerization of PDX initiated by aluminum triisopropoxide in bulk. The first question to be addressed focuses on the thermodynamics of PDX polymerization. Until a very recent paper from Nishida et al.,[15] only an estimation of the thermodynamics parameters was available and derived from the measurements of the heat capacities and enthalpies of combustion of both PDX and PPDX.[16] In this study, the thermodynamics of PDX polymerization have been quantified from the temperature dependence of the concentration in monomer at equilibrium. Furthermore, kinetic experiments on PDX polymerization initiated by $Al(O^iPr)_3$ have been conducted at 80 °C for various monomer-to-initiator ratios. These data were treated according to a reversible polymerization/depolymerization mechanism in order to

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determine the kinetic orders in both monomer and initiator as well as to estimate the absolute rate of polymerization. Finally, the mechanism of PDX ring-opening polymerization is discussed.

Experimental Section

Materials. Tri-*n*-octylmethylammonium chloride (TOAC) and trichloroacetylisocyanate (TCAI) were purchased from Acros and Sigma, respectively, and used without any further purification. Toluene was dried by refluxing over calcium hydride and distilled just before use. 1,4-Dioxan-2-one (PDX) was kindly provided by the Department of Chemical Engineering, Michigan State University. Crude PDX was first introduced into a previously flamed-dried two-necked, round-bottom flask under a nitrogen flow and mixed with dry toluene (10 wt/vol %). This solution was heated to 100 °C until complete dissolution, then cooled to 50 °C, and added under a nitrogen flow with calcium hydride. After 24 h, toluene and PDX were distilled under reduced pressure ($\sim 10^{-1}$ mbar). Purified PDX was finally recovered as a solid after selective toluene volatilization under reduced pressure at 0 °C and stored under nitrogen atmosphere (recovery yield $\approx$ 80%). Aluminum triisopropoxide ($Al(O^iPr)_3$) from Aldrich was purified by distillation under reduced pressure and rapidly dissolved in dry toluene as previously reported by some of us.[17] The accurate concentration of the initiator solution was determined by back-complexometric aqueous titration of Al^{3+} with standard solutions of Na_2EDTA and $ZnSO_4$ at pH 4.8.[17]

Bulk Polymerization of 1,4-Dioxan-2-one (PDX). The bulk polymerization of PDX was carried out in previously flamed-dried and nitrogen-purged 20 mL glass ampules equipped with a three-way stopcock capped with a rubber septum. These ampules were filled with ca. 5 g of purified and dried PDX, which was transferred in the melt state (T_m of PDX = 28 °C) through a previously flamed-dried stainless steel capillary under a nitrogen flow. Then, the ampules were thermostated in an oil bath between 60 and 150 °C. Once the reaction medium is thermostated at the desired temperature, the initiator solution ($Al(O^iPr)_3$) is added with a syringe and stainless steel capillary to reach initial monomer-to-Al molar ratios of 200, 400, and 600. After a predetermined polymerization time, the ampules were rapidly cooled to room temperature, and their contents were dissolved in hot 1,2-dichloroethane. Poly(1,4-dioxan-2-one) (PPDX) was then selectively precipitated into 8 vol of an ether−heptane (4:1) mixture to determine monomer conversion by weighing the dried poly(ester-*alt*-ether). In a next step, aluminum residues were extracted as previously reported.[14] Reproducibility of the polymerization reaction and polymer recovery method has been checked by repetitive experiments, which give monomer conversion values with relative error estimated to maximum ±3%.

Characterization. ^1H NMR spectra were recorded using a Bruker AMX-300 apparatus in 1,1,2,2-tetrachloroethane-d_2 (60 mg/0.6 mL). Size exclusion chromatography (SEC) of poly(1,4-dioxan-2-one) was performed in $CHCl_3$ containing 0.3 wt % of TOAC at 40 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 0.6 mL/min), a manual injector (loop volume = 200 μL, solution concentration = 1 mg/mL), a PL-DRI refractive index detector, and four columns: a PL gel 10 μm guard column and three PL gel Mixed-B 10 μm columns. Molecular weights and molecular weight distribution were calculated with reference to polystyrene standards.

Results and Discussion

Thermodynamics. In a first series of experiments, the ring-opening polymerization (ROP) of 1,4-dioxan-2-one (PDX) has been initiated by aluminum triisopropoxide ($Al(O^iPr)_3$) in bulk, i.e., in the absence of solvent, for a constant initial monomer-to-initiator molar ratio ($[PDX]_0/[Al(O^iPr)_3]$) of 600 and at a temperature ranging from 60 to 150 °C. It is worth mentioning that the melting temperature (T_m) of poly(1,4-dioxan-2-one) (PPDX) is close to 110 °C while T_m of PDX is 28 °C. As reported previously,[14] the bulk polymerization of PDX proceeds very rapidly when initiated by $Al(O^iPr)_3$ at 100 °C for various initial monomer-to-Al molar ratios. For an initial $[PDX]_0/[Al]$ ratio of 600, the time dependence of monomer consumption passes through a maximum after about 7 min, and then the monomer conversion decreases and levels off at a value close to the equilibrium monomer concentration within 12 min. Such a behavior is in perfect agreement with previously reported data on the bulk polymerization of PDX promoted by zinc salts, even though the time required to reach maximum monomer conversion is extended to several hours.[12] Table 1 shows the temperature dependence of the equilibrium monomer conversion expressed in weight percent after 14 h of polymerization, i.e., after a period of time long enough to be at the thermodynamic equilibrium. In practice, these values have been determined by weighing the PPDX chains recovered by dissolution of the crude polymerization product into hot 1,2-dichloroethane, followed by selective precipitation into an ether−heptane (4:1) mixture. The monomer conversions reached at equilibrium decrease with increasing polymerization temperature. It is also worth mentioning that crystallization of the crude reaction medium occurs at temperature lower than 110 °C, at least within 14 h.

Table 1. Effect of Polymerization Temperature on the Monomer Conversion Reached at Equilibrium for a $[PDX]_0/[Al(O^iPr)_3]$ Ratio of 600 and a Polymerization Time of 14 h

polym temp (°C)	equilib monomer conv (wt %)	polym temp (°C)	equilib monomer conv (wt %)
60	91	110	70
80	88	120	70
90	75	135	66
100	75	150	57

As well-known, the polymerization of PDX leaves high amounts of unreacted monomer due to a quite low ceiling temperature. Such a monomer−polymer equilibrium can adequately be described by the microreversibility model according to which all growing chains (M_n* and M_{n+1}*) are capable of depolymerizing until they reach a constant monomer equilibrium concentration (eq 1).

$$M_n^* + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^* \qquad (1)$$

where k_p and k_{dp} correspond to the propagation rate constant and the depolymerization rate constant, respectively.

Assuming an equal reactivity among the active centers and a total number of active centers equivalent to the initial number of initiator molecules, the monomer equilibrium concentration ($[M_e]$) can be efficiently expressed by Dainton's equation (eq 2).[18]

$$R \ln[M_e] = R \ln\left(\frac{k_{dp}}{k_p}\right) = \frac{\Delta H_p}{T} - \Delta S_p^0 \qquad (2)$$

where ΔH_p is the enthalpy of polymerization under the prevailing experimental conditions, ΔS_p^0 is the entropy change at the standard state ($[M_e] = 1$ mol L^{-1}), and R is the perfect gas constant. To express $[M_e]$ in mol L^{-1}, it has been referred to the densities of PDX monomer

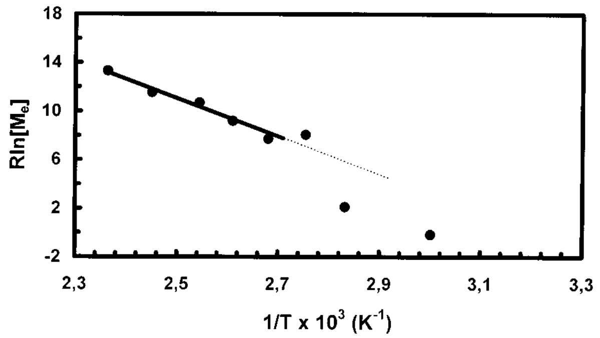


Figure 1. Plot of R ln[M_e] vs $1/T$ (K^{-1}) as calculated in bulk polymerization of PDX initiated by Al(O^iPr)$_3$ (reaction time of 14 h). Below ca. 110 °C, i.e., above $1/T$ of ca. 2.65×10^{-3} K^{-1}, PPDX gradually crystallized.

and PPDX in either crystalline or melt state as measured by dilatometry at temperatures ranging from 30 to 180 °C by Nishida et al.[15] (eqs 3−5).

$$\rho_{\mathrm{PDX}} = 1.273 - 1.197 \times 10^{-3} T\ (°\mathrm{C}) + 1.027 \times 10^{-6} T\ (°\mathrm{C})^2 \quad (3)$$

$$\rho_{\mathrm{melt\ PPDX}} = 1.368 - 9.664 \times 10^{-4} T\ (°\mathrm{C}) \quad (4)$$

$$\rho_{\mathrm{crystallized\ PPDX}} = 1.406 - 7.071 \times 10^{-4} T\ (°\mathrm{C}) \quad (5)$$

Figure 1 shows the linear regression analysis performed by plotting R ln[M_e] vs $1/T$. It results a straight line at least for polymerizations performed at temperature higher than the PPDX melting temperature. Above ca. 110 °C, the enthalpy and standard entropy of polymerization are -15.8 kJ mol^{-1} and -50.4 J mol^{-1} K^{-1}, respectively. These values, which are respectively calculated from the slope and the Y value at the zero point of the linear regression of R ln[M_e] vs $1/T$, are in quite good agreement with those reported by Nishida et al. using either Sn(Oct)$_2$ or triethylaluminum to promote the PDX polymerization in bulk: $\Delta H_p = -14.1$ kJ mol^{-1} and $\Delta S_p^0 = -45.3$ J mol^{-1} K^{-1}.[15] This confirms if need be that the equilibrium monomer concentration is independent of the initiator nature. Resolving eq 2 so that [M_e] is equal to the initial monomer concentration, [M_0], a ceiling temperature, T_c, of 235 °C can be estimated. Furthermore, an entropy of polymerization under the prevailing experimental conditions, ΔS_p, of -31 J mol^{-1} K^{-1} can also be calculated from the $\Delta H_p/T_c$ ratio. Below 110 °C, PPDX gradually crystallizes with increasing monomer conversion and reaction time. This is evidenced by the growing opacity of the reaction medium in the course of the polymerization and the break in the semilogarithmic plot (Figure 1). The crystallization of PPDX chains is responsible for an increase in the concentration of both the residual monomer and the active aluminum alkoxides species in the amorphous regions. Consequently, the global [M_e] decreases. Such a behavior has already been observed during the polymerization of LL-lactide at temperatures lower than the melting temperature of the corresponding polyester. Shinno et al. have even taken advantage of the crystallization of poly(LL-lactide) to extend the polymerization degree by a postpolymerization treatment at a temperature lower than the melting temperature.[19]

Table 2. Influence of Polymerization Time and [PDX]$_0$/[Al(O^iPr)$_3$] Ratio on Monomer Conversion and PPDX Molecular Weight Distribution As Obtained in Bulk at 80 °C

entry	[PDX]$_0$/[Al]	polym time (min)	PDX conv^a (%)	M_n^{b}	M_w/M_n^{b}
1	200	3	31	2900	1.23
2	200	7	59	5300	1.26
3	200	12	59	5500	1.24
4	200	15	82	6900	1.22
5	400	5	11	2500	1.29
6	400	15	46	4200	1.20
7	400	25	72	6000	1.14
8	400	31	79	8800	1.23
9	600	12	30	3200	1.19
10	600	21	58	7000	1.20
11	600	30	73	11200	1.13
12	600	40	87^c	—^{d}	—^{d}

[a] As determined by gravimetry (see Experimental Section). [b] As determined by SEC with reference to polystyrene standards (in CHCl$_3$ + 0.3 wt % TOAC at 40 °C). [c] Crystallization of PPDX took place after 35 min of polymerization. [d] Sample partially insoluble in CHCl$_3$ added with 0.3 wt % TOAC at 40 °C.

Kinetics. Table 2 shows the effect of the initial monomer-to-Al molar ratio and reaction time on the monomer conversion and PPDX molecular weight distribution for polymerization conducted at 80 °C. Although the temperature is lower than the melting temperature of crystalline PPDX fraction ($T_m \sim 110$ °C), the bulk polymerization proceeds homogeneously at 80 °C, at least up to 35 min of polymerization. Beyond this period of time, crystallization starts to take place as evidenced by the gradual opacity of the reaction medium.

Whatever the [PDX]$_0$/[Al(O^iPr)$_3$] ratio, both monomer conversion and PPDX molecular weight (with reference to polystyrene standards) increase gradually with time, except for the last entry in Table 2. In this specific sample, crystallization of PPDX has already occurred after 35 min of polymerization. As a result, the resulting PPDX sample could not be fully solubilized for its characterization by GPC. Furthermore, it is worth pointing out the relative increase of the number-average molecular weight, M_n, with the [PDX]$_0$/[Al(O^iPr)$_3$] ratio at constant monomer conversion. As an example, M_n passes from 6000 to 11 200 for [PDX]$_0$/[Al(O^iPr)$_3$] ratios of 400 and 600, respectively (Table 2, entries 7 and 11). Striking features are the low values of the apparent molecular weight as expressed with reference to polystyrene standards and the quite narrow polydispersities ($M_w/M_n < 1.3$) observed by using chloroform added with 0.3 wt % of TOAC as an eluent at 40 °C (Figure 2). With this respect, it is worth recalling the poor solubility of PPDX in conventional organic solvents. It gives credit to the formation of very compact coils characterized by a low hydrodynamic volume compared to highly soluble polystyrene. Even though absolute molecular weight determination would be strictly necessary to draw definitive conclusions, it comes out that aluminum alkoxides likely behave as the actual initiators, in agreement with the increase of inherent viscosities in function [PDX]$_0$/[Al(O^iPr)$_3$] ratio as previously reported.[14]

Figure 3 compares the time dependence of monomer consumption measured at 80 °C for three different initial PDX-to-Al molar ratios. A polymerization conducted at 100 °C for an initial monomer-to-Al molar ratio of 600 is also shown. It highlights that the time dependence of monomer consumption shows an evolu-

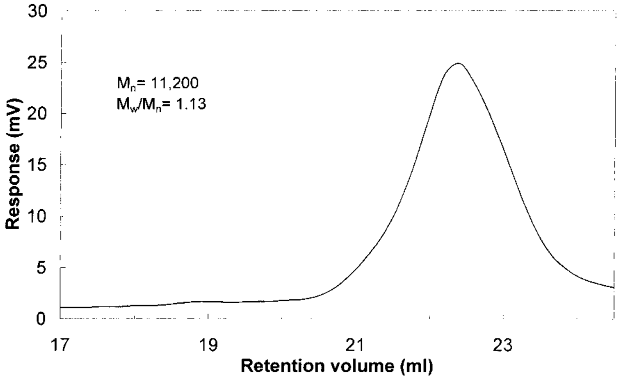


Figure 2. Typical GPC trace of a PPDX sample as synthesized in bulk at 80 °C (entry 11, Table 2). Solvent: $CHCl_3$ added with 0.3 wt % of TOAC (at 40 °C, see Experimental Section).

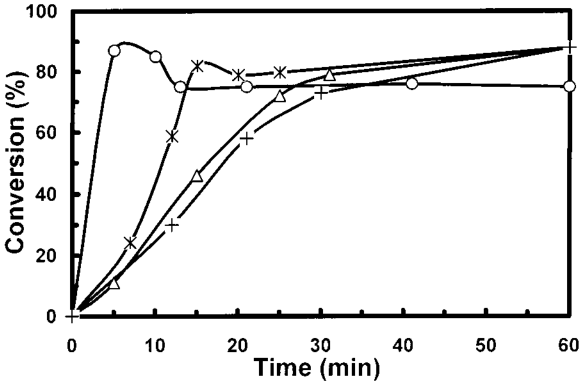


Figure 3. Time dependence of monomer conversion in the bulk polymerization of PDX carried out at 100 °C for a $[PDX]_0/[Al(O^iPr)_3]$ ratio of 600 (○) and at 80 °C for $[PDX]_0/[Al(O^iPr)_3]$ ratio of 200 (∗), 400 (△), and 600 (+), respectively.

tion strictly dependent on both temperature and $[PDX]_0/[Al(O^iPr)_3]$ ratio. Indeed, either the monomer consumption can gently increase up to reach thermodynamic equilibrium or it can first pass through a maximum, then decrease, and level off. Such a behavior is in perfect agreement with previously published data. For instance, it correlates with the time–conversion curve of $Zn(Lac)_2$-catalyzed polymerization of PDX at 100 °C (for a $[PDX]_0$/[benzyl alcohol] of 25) which passes through a maximum,[12] but also with smooth time–conversion curves of PDX polymerization with triethylaluminum at 80 °C (for a $[PDX]_0/[Al]$ ratio of 1960 and with $Sn(Oct)_2$ at 80 and 120 °C for a $[PDX]_0/[Sn]$ ratio of 4900).[15] It is useful to recall that $Sn(Oct)_2$-catalyzed bulk polymerization of PDX is relatively fast compared to $Zn(Lac)_2$-catalyzed one, but aluminum derivatives are much more efficient. Note that similar kinetic observations have already been reported for the bulk polymerization of lactides initiated by aluminum alkoxides[20] and $Sn(Oct)_2$.[21]

The very fast polymerization of PDX initiated by $Al(O^iPr)_3$ in bulk prompts us to carry out further mechanism and kinetic investigations at 80 °C. The kinetics of propagation for an equilibrium polymerization system can be adequately expressed by eq 6.

$$\ln\left(\frac{[M_0]-[M_e]}{[M_t]-[M_e]}\right) = k_{app}t \qquad (6)$$

where $[M_0]$ is the initial monomer concentration, $[M_e]$ is the equilibrium monomer concentration, $[M_t]$ is the actual monomer concentration at time t, and k_{app} is the apparent rate constant. $[M_0]$ and $[M_t]$ were calculated from the monomer conversion expressed in wt % and from the densities of the monomer (eq 3) and of the corresponding molten polymer (eq 4). It has thus been taking into account that, within a polymerization time lower than 35 min at 80 °C, the reaction medium remains homogeneous and that no crystallization occurs. $[M_e]$ has been calculated according to eq 2 with $\Delta H_p = -15.8$ kJ mol^{-1} and $\Delta S_p^0 = -50.4$ J mol^{-1} K^{-1}.

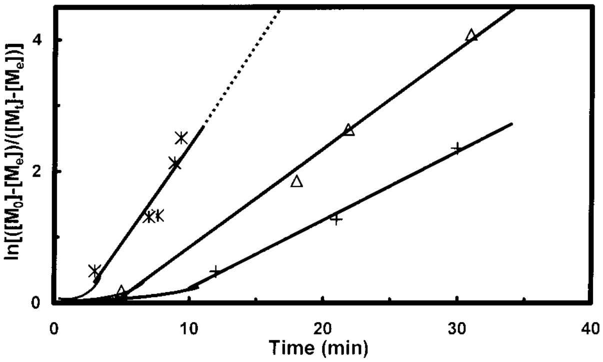


Figure 4. Time dependence of $\ln\{\{([M_0] - [M_e])\}/\{([M_t] - [M_e])\}\}$ in the bulk polymerization of PDX initiated by $Al(O^iPr)_3$ at 80 °C for $[PDX]_0/[Al]$ ratios of 200 (∗), 400 (△), and 600 (+).

Figure 4 shows the semilogarithmic plot for various initial monomer-to-Al molar ratios. Whatever $[PDX]_0/[Al(O^iPr)_3]$, a linear time dependence of $\ln\{\{([M_0] - [M_e])\}/\{([M_t] - [M_e])\}\}$ is observed after an induction period close to 6 min. This induction period can be attributed to the rearrangement of $Al(O^iPr)_3$ and the formation of the actual active species.[22] The linearity of the relationship in Figure 4 attests that the bulk polymerization kinetics of PDX initiated by $Al(O^iPr)_3$ is first order in monomer in the overall range of monomer conversion investigated, at least for the $[PDX]_0/[Al(O^iPr)_3]$ ratios of 400 and 600 at 80 °C. When the initial-to-monomer molar ratio is 200, the linearity is verified for conversion lower than 40%. Such a linear dependence also indicates that the number of growing chains does not appreciably change during polymerization in the prevailing experimental conditions, in agreement with the narrow molecular weight distribution of the polyester chains. The slope of the linear relationships enables to determine k_{app} values of 0.293, 0.144, and 0.104 min^{-1} for $[PDX]_0/[Al(O^iPr)_3]$ ratios of 200, 400, and 600, respectively. The order in initiator, a, and the absolute rate constant, k_p, have then been tentatively approached by assuming that $k_{app} = k_p[Al(O^iPr)_3]^a$. In practice, a regression on $\ln(k_{app})$ vs $\ln[Al(O^iPr)_3]$ has been performed knowing the initial initiator concentrations. It results a first order in initiator ($a = 0.95$) and a k_p value of 0.08 L mol^{-1} s^{-1} when the polymerization of PDX is initiated by $Al(O^iPr)_3$ at 80 °C in bulk. It is worth pointing out that the absolute rate constant is in the same range than the k_p value determined by Nishida et al. for the bulk polymerization of PDX initiated by $AlEt_3$ at 80 °C ($k_p = 0.055$ L mol^{-1} s^{-1}).[15]

As might be evidenced from the time dependence of monomer consumption for $[PDX]_0/[Al(O^iPr)_3]$ ratios of 200 at 80 °C and 600 at 100 °C (see Figure 3), some questions are still pending on the actual nature and composition of the polymerization products, particularly

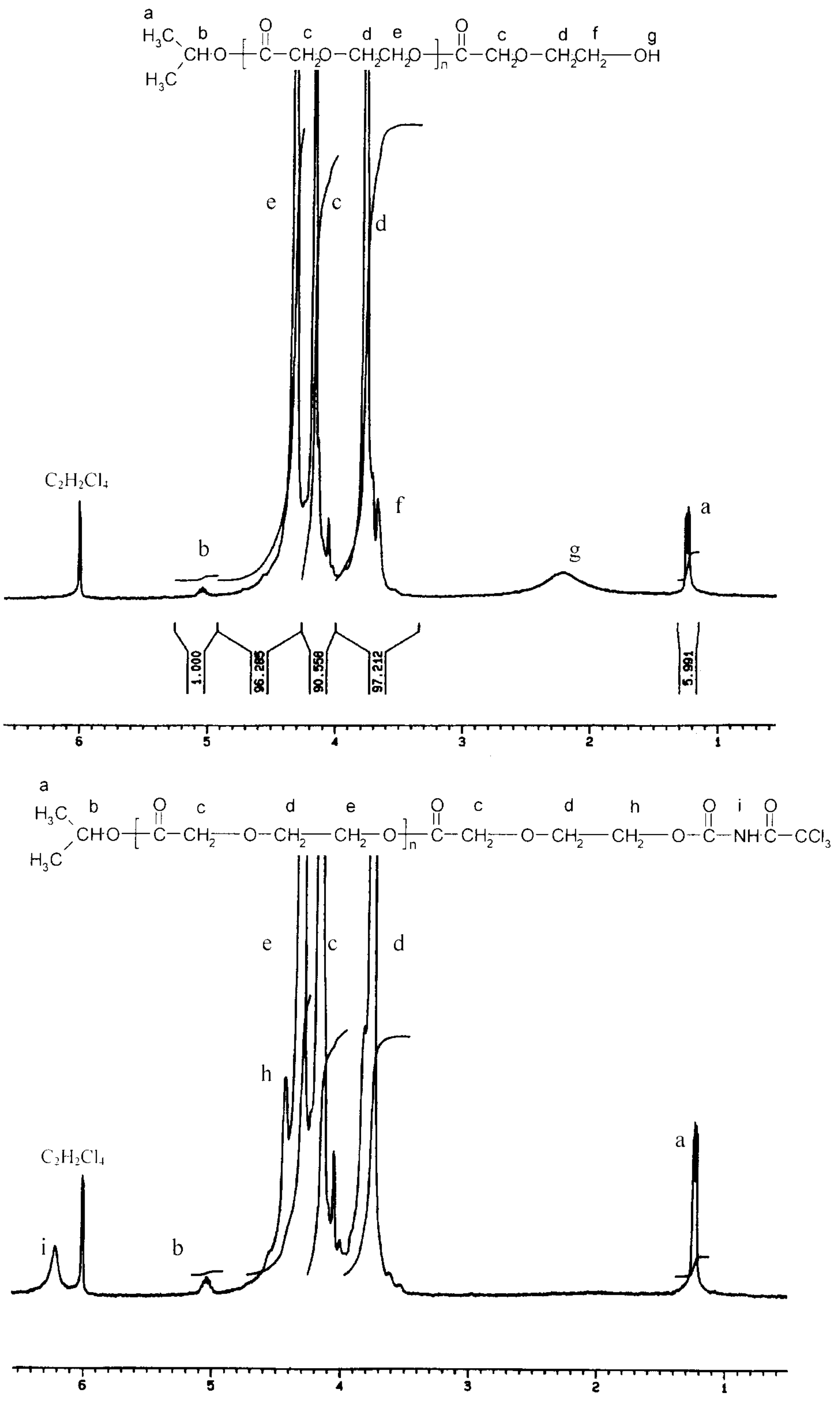
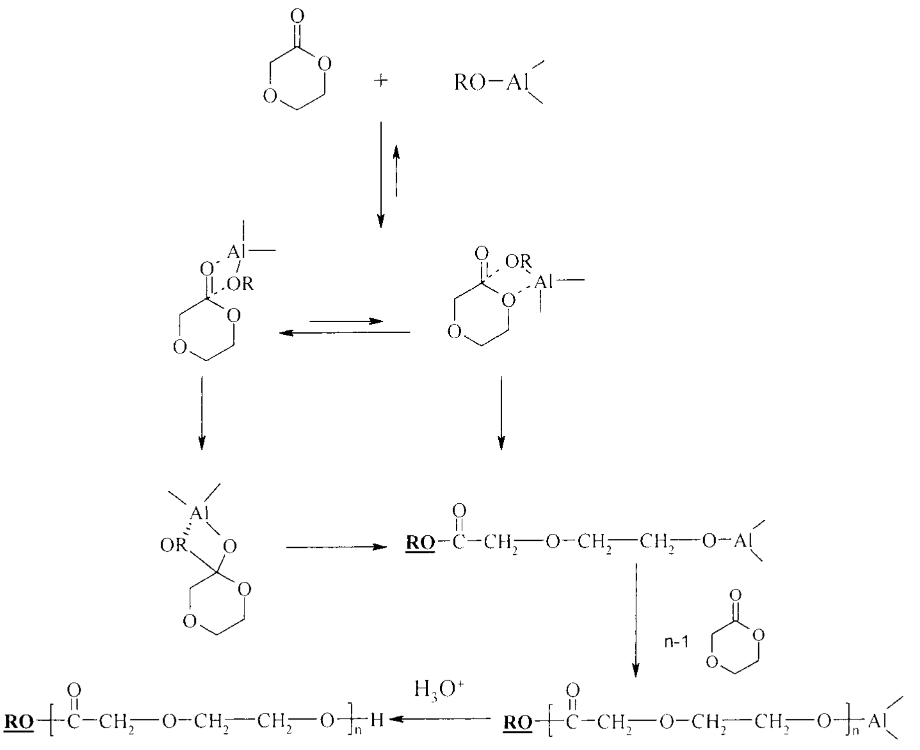


Figure 5. ^{1}H NMR spectra of α-isopropoxy, *ω*-hydroxyl-PPDX (a, top) (Table 2, entry 1) and α-isopropoxy, *ω*-trichloroacetylcarbamate-PPDX (b, bottom) in deuterated 1,1,2,2-tetrachloroethane.

close to the maxima. Indeed, one cannot exclude the presence of cyclic oligomers together with linear chains. A more detailed analysis is expectedly under current investigation.[23]

Mechanism. To determine the mechanism of the ring-opening polymerization of PDX initiated by $\mathrm{Al(O^iPr)_3}$ at 80 °C in bulk, an oligomer of the resulting poly(ester-*alt*-ether) has been solubilized, and the aluminum active species have been hydrolytically deactivated and finally eliminated by complexometric extraction with EDTA. Figure 5a shows the ^{1}H NMR spectrum of a PPDX obtained after 3 min of polymerization in bulk at 80 °C for a $\mathrm{[PDX]_0/[Al(O^iPr)_3]}$ ratio of 200 (Table 2, entry 1). In addition to the methylene protons of the repetitive units at 3.80, 4.20, and 4.38 ppm (see assignation directly in Figure 5), four minor resonances could be assigned to an isopropylester end group ($\delta(\mathrm{C}H_3)_2\mathrm{CH{-}O{-}C(O){-}} = 1.23$ ppm and $\delta(\mathrm{CH_3})_2$-

Scheme 1



C*H*−O−C(O)− = 5.04 ppm) and to an hydroxyl end group (δ*H*O− = 2.20 ppm and δ−CH_2−OH = 3.67 ppm). No carboxylic acid proton could be detected. Since the α-hydroxymethylene protons overlap the methylene protons of the repetitive units at 3.80 ppm, they cannot be resolved. In an attempt to separate these signals, a drop of trichloroacetylisocyanate (TCAI) was added directly in the NMR tube. TCAI is known to quantitatively react with hydroxyl functions to form trichloroacetylcarbamate derivatives, thereby causing a downfield shift of approximately 1 ppm for the α-hydroxymethylene protons.[24] Figure 5b shows that signals assigned to the hydroxyl end group have totally disappeared to the benefit of methylene protons in the α position of a trichloroacetylcarbamate function at 4.43 ppm. All these observations demonstrate that the polymerization of PDX initiated by $Al(O^iPr)_3$ actually proceeds through a coordination−insertion mechanism with an endocyclic O−acyl rupture of the monomer bond (Scheme 1).

Assuming that each poly(ester-*alt*-ether) chain is selectively end-capped by an isopropyl ester group, an experimental mean degree of polymerization of 49 can be calculated from the relative intensities of the methylene protons of the repetitive units (Hd) and the methyl protons of the isopropoxy group (Ha/3). The theoretical mean degree of polymerization is given by the product of the initial monomer-to-Al molar ratio and the monomer conversion, i.e., $200 \times 0.31 = 62$ (Table 2, entry 1). It comes out that all aluminum alkoxide functions are not active, but only 1.3 (62/49) alkoxides, on average, per $Al(O^iPr)_3$ effectively initiate the polymerization. It is worth noting that this value is very close to the average number of alkoxide groups per Al reported for the polymerization of ϵ-caprolactone (CL) by $Al(O^iPr)_3$ at 100 °C.[22] A pertinent explanation was found by Duda and Penczek[25] in the difference of reactivity between the tetrameric (A4) and the trimeric (A3) $Al(O^iPr)_3$ species known to coexist in the thermodynamic equilibrium. A3 is by far more reactive than A4. When CL or PDX polymerization is initiated by the A3/A4 mixture, A3 is completely consumed whereas A4 remains unreacted. In other words, the A3/A4 mixture used as the initiator at given temperature and concentration has a composition such that the selective initiation by the three isopropoxide groups of A3 fits the experimental observation, i.e., on average 1.3 active sites per Al atom (from A3 + A4). Note that such an explanation has been confirmed by the controlled synthesis of P(CL-*b*-PDX) block copolymers by successive addition of the comonomers onto $Al(O^iPr)_3$. No homopolymers have been recovered in perfect agreement with an equal number of active sites per Al whatever the monomer in presence.[14]

Conclusions

To our best knowledge, it is the first time that commercially available aluminum alkoxides such as aluminum triisopropoxide are used as initiators for the bulk polymerization of 1,4-dioxan-2-one (PDX). Compared to the large amount of organometallic compounds acting as catalysts while the active species are hydroxyl containing compounds, and compared to $AlEt_3$, $ZnEt_2$, or $Sn(Oct)_2$ which are just precursors of the true initiators by reacting with free hydroxyl compounds remaining in the crude monomer, $Al(O^iPr)_3$ has proved to behave as the actual initiator in the polymerization of highly purified PDX. The ring-opening polymerization proceeds through a coordination−insertion mechanism with O−acyl rupture of the endocyclic ester bond of the monomer. It has also been shown that the rate of the bulk polymerization of PDX initiated by $Al(O^iPr)_3$ follows a conventional kinetics which is of first order in both monomer and initiator and with an absolute rate constant of 0.08 L mol^{-1} 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 ($M_w/M_n < 1.3$). A treatment at 80 °C for a longer period of time allows to reduce the amount of unreacted monomer from 20 to 12 wt %, values corresponding to the thermodynamic equilibrium in the melt and crystalline states, respectively. Above 80 °C, the polymerization deviates from this reactive scheme so that monomer conversion passes through a maximum and then decreases for leveling off at the thermodynamic equilibrium monomer conversion.

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