Monomer−Linear Macromolecules−Cyclic Oligomers Equilibria in the Polymerization of 1,4-Dioxan-2-one

Jan Libiszowski,[†] Adam Kowalski,[†] Ryszard Szymanski,[†] Andrzej Duda,*[,†] Jean-Marie Raquez,[‡] Philippe Degée,[‡] and Philippe Dubois*[,‡]

Department of Polymer Chemistry, Center of Molecular and Macromolecular Studies (CMMS), Polish Academy of Sciences, Sienkiewicza 112, PL-90-363 Lodz, Poland, and Laboratory of Polymeric and Composite Materials (LPCM), University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium

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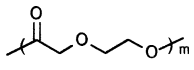
ABSTRACT: 1,4-Dioxane-2-one (DX) was polymerized in 1,4-dioxane as solvent or in bulk by means of the tin octoate/butyl alcohol ($Sn(Oct)_2$/BuOH) mixture as an initiating system, in the range of temperatures from 80 to 120 °C. Size exclusion chromatography (SEC) and MALDI TOF mass spectrometry measurements of the crude reacting mixtures revealed that in the thermodynamically equilibrated systems a relatively high fraction of cyclic oligomers (DX(i)) appear. The molar concentration of cyclic oligomers ($\sum i[DX(i)]_{eq}$) increased with increasing temperature and monomer concentration in the feed and reached a maximum value equal approximately to 1 mol L^{-1} for the polymerization in bulk. On the other hand, the mass fraction (f) of cyclic oligomers after passing a maximum ($f = 40\%$ at $[DX]_0 \approx 4.0$ mol L^{-1}, 100 °C) decreased with increasing $[DX]_0$, and eventually for bulk polymerization $f < 10\%$ ($f = 8\%$ at 80 °C) was reached. The equilibrium monomer concentration, determined by means of SEC, increased with increasing $[DX]_0$ until $[DX]_0 \approx 4.0$ mol L^{-1} when it became constant value ($[DX]_{eq}$). The temperature dependence of thus-determined $[DX]_{eq}$ gave the following thermodynamic parameters of polymerization: $\Delta H_p = -13.8$ kJ mol^{-1} and $\Delta S_p° = -45.0$ J mol^{-1} K^{-1}. Thermodynamic parameters of polymerization of cyclic oligomers (DX(i), $i = 3-8$) have also been determined in a similar way.

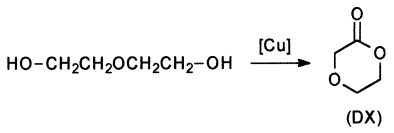
Introduction

Poly(1,4-dioxan-2-one) (PDX)−poly(aliphatic ester-*alt*-ether)—is a thermoplastic, biocompatible, and biodegradable material.



(PDX)

1,4-Dioxan-2-one (DX) homo- and copolymers have already been used in various biomedical applications, for example as monofilament sutures, bone and tissue fixation devices, or drug delivery systems.[1] Recently, a convenient one-step synthesis of the DX monomer, starting from an inexpensive substrate−diethylene glycol, has been elaborated (eq 1).[2]



(DX) (1)

The latter opens a door to the large-scale applications of PDX as a commodity thermoplastic, degrading rapidly in the environment when discarded after required time of exploitation.

The first reports on DX polymerization come from the early 1960s,[3] but the more systematic studies on the polymerization mechanism have been started only recently. The best polymerization control was achieved with covalent multivalent metal (Mt = Al, Sn(II), Sn(IV), Zn, etc.) alkoxides or carboxylates as (co)initiators.[1,4−9]

The polymerization proceeds similarly to that with other cyclic esters (for example, lactides or ϵ-caprolactone).[10,11] Independent of the initiator used (alkoxide or carboxylate), the involved active centers are expected to have the covalent metal alkoxide structures. Elementary chain-growth reaction consists of the concerted monomer insertion into the alkoxide oxygen−metal bond followed by the acyl−oxygen bond scission and reformation of the alkoxide species.[4,7] Molar mass (M_n) of the resulting PDX was claimed to be controlled by a ratio of concentrations of the monomer consumed and the alkoxide group in the feed ($M_n = 102.09([DX]_0 - [DX])/[RO]_0$, where 102.09 is DX molar mass).

The equilibrium concentration of DX monomer ($[DX]_{eq}$) is relatively high because of the medium ring strain, thus $\Delta H_p \cong -15$ kJ mol^{-1}.[8,9,12] The molar fraction of the unreacted DX can be, however, reduced by aging the living polymerization mixtures below melting temperature of PDX (110 °C). Under these conditions PDX crystallizes, and a volume of the amorphous phase, in which the unreacted DX still remains, decreases at the same time. That is why [DX] increases above $[DX]_{eq}$, and then an additional monomer consumption proceeds, leading to the apparent decrease of $[DX]_{eq}$ (actually molar fraction of DX).[9] Similar behavior has also been reported for the polymerization of LL-lactide.[13]

The intramolecular transesterification (called also backbiting) leads to formation of cyclic oligomers. The polymerization control with regard to M_n and end groups may be lost this way. On the contrary, the intermolecular transesterification does not change M_n and results only in the segmental exchange of the polyester chains, leading to a gradual broadening of the molar mass distribution with increasing monomer conversion and eventually to M_w/M_n equal to 2.

[†] Polish Academy of Sciences.
[‡] University of Mons-Hainaut.
* Corresponding authors. E-mail: A.D., anduda@bilbo.cbmm.lodz.pl; P.D., philippe.dubois@umh.ac.be.

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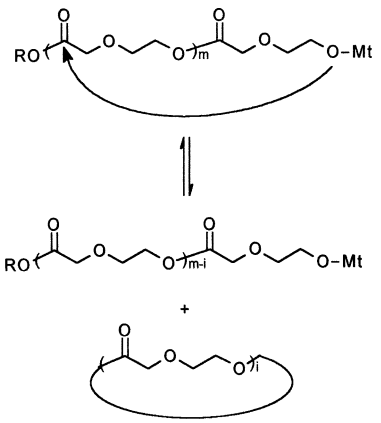
Similar reactions of chain transfer have been already studied in polymerizations of other cyclic esters (most extensively for ϵ-caprolactone (CL) and LL-lactide (LA)), and the pertinent rate constants have been determined.[14−20] The extent of a given kind of transfer, for the thermodynamically equilibrated systems, depends on the monomer (actually on the repeating unit) structure. For example, in CL polymerization both intra- and intermolecular transesterifications play equally important role whereas for LA only intermolecular transesterification is significant. Interestingly enough, these side reactions can kinetically be depressed or even practically eliminated when the less reactive and thus more selective initiators are applied.[17,18,21]

Results reported in the present work show, for the first time to the best of our knowledge, that in the thermodynamically equilibrated DX/PDX system significant fraction of cyclic oligomers is formed:



(2)

We analyze extent of this side reaction more in detail as a function of the starting monomer concentration and of the polymerization temperature.

Furthermore, a practically important feature of DX polymerization, hampering direct analysis of the polymerization mixtures, is the insolubility of the resulting high molar mass PDX at ambient temperatures in solvents used usually in anionic coordination (pseudoanionic) polymerization. Therefore, this paper aims at reporting on thermodynamics of polymerization and macrocyclization phenomena in the DX/tin octoate/butyl alcohol model system with 1,4-dioxane as a solvent. This system provides a convenient possibility of adjusting molar masses of PDX low enough to govern the homogeneity of polymerization mixtures even at room temperature as well as enables MALDI TOF measurements.

Experimental Section

Materials. 1,4-Dioxan-2-one (DX), prepared as described in ref 2, was a gift from the Department of the Chemical Engineering, Michigan State University. Crude DX monomer was dried over CaH_2 at 40 °C for several hours, purified by vacuum distillation ($\approx 10^{-2}$ mbar, 80 °C), and distributed into calibrated ampules equipped with break-seals, which were eventually sealed off. Tin(II) octoate ($Sn(Oct_2)$) (95%, according to our determination[22]) and butyl alcohol (BuOH) (99.4+%) purchased from Aldrich were purified as described in ref 22. 1,4-Dioxane (99%), from POCh (Gliwice, Poland), was kept over KOH during several days, then distilled on sodium cuts, distilled again, and stored over sodium−potassium liquid alloy in glass ampules equipped with Teflon stopcocks. Methylene chloride (99%) and tetrahydrofuran (99%) from POCh (Gliwice, Poland) and 1,1,2,2-tetrachloroethane (99%), from Aldrich, were purified by distillation from CaH_2.

Polymerization Procedures. Polymerizing mixtures were prepared in sealed glass ampules using standard high-vacuum technique. A general procedure follows the example described below. $Sn(Oct)_2$ (1 mL of 0.15 mol L^{-1} solution in 1,4-dioxane (6.08×10^{-2} g)) and DX (6.6 g (64.65 mmol)) were transferred under vacuum into break-seals and sealed after freezing in liquid nitrogen. Butyl alcohol (BuOH) (0.167 g (2.25 mmol)) was distilled into a thin-walled phial and then sealed after freezing in liquid nitrogen. Break-seals containing $SnOct_2$/1,4-dioxane solution and DX monomer, tube with immersed BuOH phial, and glass ampules were sealed to the reaction glass vessel (≈30 mL) equipped with three glass ampules (≈3 mL). 1,4-Dioxane (8.6 mL) was distilled into the resulting reactor, which was then sealed off. The break-seals and phial were broken and when all components were dissolved at room temperature; the resulting solution was transferred into the glass ampules. The ampules containing reacting mixture were then sealed off and placed into thermostat and kept 36, 24, and 12 h at 80, 100, and 120 °C, respectively. Eventually, reacting mixtures were chilled rapidly in a liquid nitrogen to room temperature, injected into a size exclusion chromatography apparatus, and analyzed on the MALDI−TOF instrument. As checked by a series of preliminary measurements, the indicated above reaction times were long enough to reach the thermodynamic equilibrium conditions, at least with regard to the concentration of the unreacted monomer and to the distribution of the cyclic oligomers. Reacting mixtures resulting from the bulk polymerizations were dissolved in 1,1,2,2-tetrachloroethane before chromatographic and mass spectrometric measurements.

Measurements of Equilibrium Monomer Concentration ($[DX]_{eq}$). $[DX]_{eq}$ were measured by means of size exclusion chromatography (SEC). SEC traces were recorded using a LKB 2150 HPLC pump and a set of two TSK Gel columns (G 2000 H_{XL} and 4000 H_{XL}) at 20 °C. A Wyatt Optilab 903 interferometric refractometer (Wyatt Technology Corp., Santa Barbara, CA) was applied as detector. Methylene chloride was used as eluent at flow rate of 0.8 mL min^{-1}. The coefficient of the RI response of the DX monomer (relative to the PDX polymer) was determined from the SEC traces of mixtures of known DX/PDX compositions—it is equal to 0.584. Thus, $[DX]_{eq} = [DX]_0\{(A_m/0.584)/(A_p + A_m/0.584)\}$, where A_m and A_p denote surface areas under the monomer and polymer signals, respectively.

MALDI TOF Measurements. Mass spectrometric measurements were performed using a Voyager-Elite (PerSeptive Biosystems, Franingham, MA) time-of-flight instrument equipped with a pulsed N_2 laser (337 nm, 4 ns pulse width) and time delayed extraction ion source. An accelerating voltage of 20 kV was used. Mass spectra were obtained in the reflector and/or linear mode. The matrix, 2,5-dihydroxybenzoic acid, and the cationizing agent (NaI) were dissolved in tetrahydrofuran in concentrations equal to 10 mg mL^{-1}, and the solution was mixed with the polymerizing mixture (monomer concentration in the feed: 1.0 mol L^{-1}) in a 25:1 v/v ratio. The mixture was dried on a stainless steel plate covered by the gold metal target.

Results and Discussion

1,4-Dioxan-2-one/Tin Octoate Bulk Polymerization. Polymerization carried out with the 1,4-dioxan-2-one/tin octoate ($DX/Sn(Oct)_2$) system in bulk and without purposely added co-initiator revealed a considerable amount of macrocyclics formed.

Figure 1 shows representative SEC trace of the crude reacting mixture obtained in the bulk polymerization in which formation of high molar mass PDX could be expected. Characteristic feature of this chromatogram is the presence of a long tail in the range from ≈15 to 18.5 mL which may be attributed to cyclic oligomers (DX(i)). We expected that more detailed insight into the composition of this low molar mass fraction should be enabled by mass spectrometry. Therefore, in the next

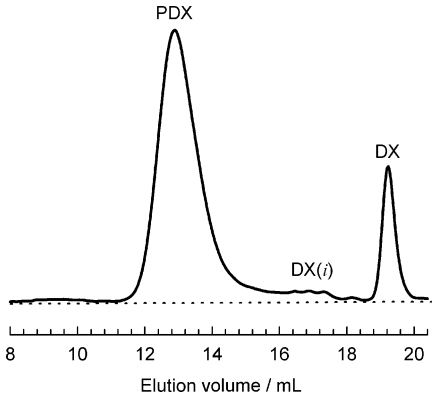
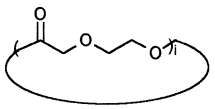


Figure 1. SEC trace of the crude 1,4-dioxan-2-one/tin octoate reacting mixture. Conditions: $[DX]_0 = 11.4$ mol L^{-1}, $[Sn(Oct)_2]_0 = 1.3 \times 10^{-2}$ mol L^{-1}, 100 °C; polymerization time = 24 h.

step of analysis the crude reacting mixture, dissolved in 1,1,2,2-tetrachloroethane, has been precipitated into tetrahydrofuran (in which high molar mass PDX is insoluble). The solvents from the separated homogeneous supernatant have been evaporated, and the solid remainder has been subjected to the MALDI TOF measurements. In the resulting spectrum, presented in Figure 2, a series of signals being apart of $m/z = 102.09$ (equivalent to DX molar mass) are clearly seen.

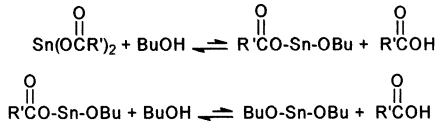


The structure to signal assignments, based on the m/z values, demonstrates the presence of one homologous series of cyclic oligomers (DX(i)) (Figure 2). The content of DX(i), expressed in concentrations of the repeating units derived from DX ($\sum i[DX(i)]$), estimated from the surface areas under the fragments of the SEC trace related to PDX, DX(i), and DX is equal to 0.9 mol L^{-1}, which is relatively high when compared to $[DX]_0 = 11.4$ mol L^{-1}. In this estimation equality of the refractive indexes for PDX and DX(i) fraction has been assumed in the first approximation. From the same SEC trace $[DX]_{eq} = 2.4$ mol L^{-1} has been determined (cf. Experimental Section), in close agreement with the values reported in refs 8 (2.5 mol L^{-1} by ^{1}H NMR) and 9 (2.6 mol L^{-1} by gravimetry).

Thus, the preliminary measurements described above point out the important role of the macrocyclization phenomena in the thermodynamically equilibrated DX/PDX systems. Moreover, in polymerization conducted in solution, when $[DX]_0$ is usually lower compared to that in bulk, the relative content of the cyclic oligomers increases, and eventually the polymerization control with respect to M_n and end groups can be lost.

Therefore, in the next part of the present work we decided to perform more systematic studies of monomer−linear polymer−cyclic oligomers equilibria in the model polymerizing system: 1,4-dioxan-2-one/tin octoate/butyl alcohol with 1,4-dioxane as a solvent.

DX/Sn(Oct)$_2$/BuOH/1,4-Dioxane Solution Polymerization. The actual initiator operating in the Sn(Oct)$_2$/cyclic ester/BuOH system has the Sn(II) mono and/or dialkoxide structure and is formed in the following exchange reactions:



where R′ stands for $C_4H_9(C_2H_5)CH$.

Moreover, BuOH acts not only as a co-initiator but also as an effective chain-transfer agent. (A more detailed analysis of mechanism of cyclic esters polymerization initiated with Sn(Oct)$_2$/BuOH mixture can be found in a series of recently published papers.[11,22−25]) For this reason molar mass of PDX (M_n(calcd), eq 4) could be predicted from the $([DX]_0 - [DX]_{eq})/[BuOH]_0$ ratio, providing that $[BuOH]_0 \gg [SnOct_2]_0$ and that only linear BuO−PDX−OH chains are formed.

$$M_n(\text{calcd}) = 102.09([DX]_0 - [DX]_{eq})/[BuOH]_0 + 74.12 \quad (4)$$

where 74.12 is the molar mass of BuOH. In the experiments described below M_n(calcd)'s have been kept below 1.5×10^3, which is in the range that polymerizing mixtures are homogeneous at room temperature. It is also important that both linear chains and cyclic oligomers can be simultaneously observed by means of MALDI TOF mass spectrometry in this M_n range.

(a) Equilibrium Monomer Concentration as a Function of $[DX]_0$. In nonideal conditions the equilib-

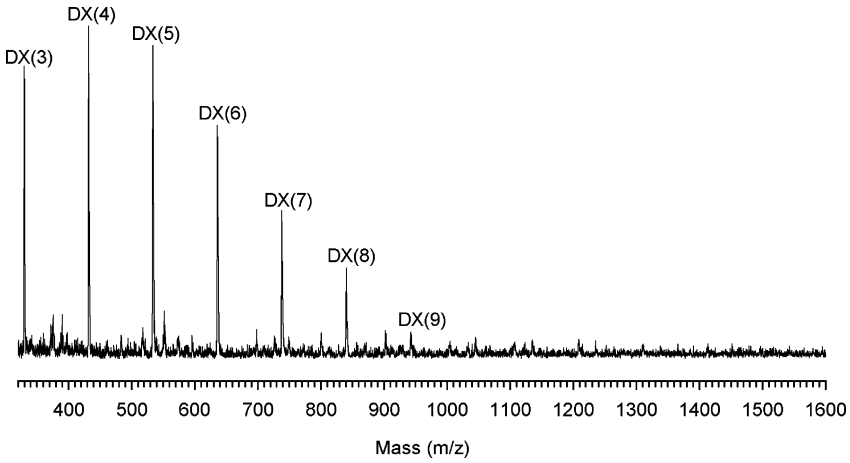
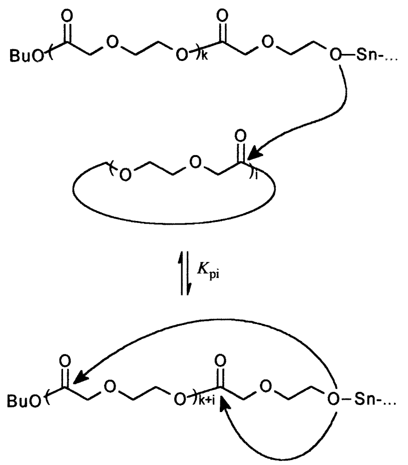


Figure 2. MALDI TOF spectrum of the tetrahydrofuran-soluble, low molar mass fraction of the 1,4-dioxan-2-one/tin octoate reacting mixture. The spectrum was registered in the linear mode; all marked signals correspond to macromolecules cationized with Na^+. Polymerization conditions are given in the caption for Figure 1.

rium monomer concentration ($[M]_{eq}$) should depend on its starting concentration ($[M]_0$), solvent, and molar mass of the linear macromolecules being in equilibrium with the monomer.[26–28] However, even when the monomer–solvent, polymer–solvent, and monomer–polymer specific interactions can be neglected, $[M]_{eq}$ increases with increasing $[M]_0$, for the $[M]_0$ values low enough, and then levels off, reaching eventually a plateau corresponding to the monomer-high polymer equilibrium. This behavior, in the case of the DX/SnOct$_2$/BuOH system, results from a concentrations balance between monomer, cyclic oligomers, and linear macromolecules:



(5)

and

$$[DX]_0 = [DX]_{eq} + \sum_{i=2}^{\infty} i[DX(i)]_{eq} + [dx]_{linear} = \frac{p}{K_{p1}} + \sum_{i=2}^{\infty} i\frac{p^i}{K_{pi}} + \frac{[BuOH]_0}{1-p} \quad (6)$$

where DX, DX(i), and dx denote monomer, cyclic i-mer, and repeating unit derived from DX, respectively; K_{p1} and K_{pi} are the pertinent equilibrium constants of propagation of monomer and cyclic i-mers, respectively; $p = (DP_n - 1)/DP_n$. A more detailed discussion of eq 6 can be found in the Appendix.

To determine a dependence of $[DX]_{eq}$ on $[DX]_0$ in solution three series of polymerization at 80, 100, and 120 °C have been carried out. In each series starting concentrations of DX was ranging from 1.4 to ≈10.9 (bulk) mol L^{-1}. Similarly, $[BuOH]_0$ was increased from 0.058 to 0.63 mol L^{-1}. After the predetermined reaction times (36, 24, and 12 h for polymerizations at 80, 100, and 120 °C, respectively) SEC measurements of the crude reacting mixtures have been performed (cf. Experimental Section). Results of these measurements are shown in Figure 3. At any temperature, $[DX]_{eq}$ increases with increasing $[DX]_0$ up to $[DX]_0 \approx 4$ mol L^{-1} and then levels off at a constant value independent of $[DX]_0$. Thus, 1,4-dioxane appears as a thermodynamically inert solvent, and also the monomer–polymer interactions can be ignored.

When the monomer–polymer–solvent interactions can be neglected, the equilibrium monomer concentration is related to the polymerization temperature by means of Dainton and Ivin's equation:[29]

$$\ln[DX]_{eq} = \frac{\Delta H_p}{RT} - \frac{\Delta S_p{}^\circ}{R} \quad (7)$$

where R is the gas constant and T the absolute temperature; ΔH_p is the enthalpy and $\Delta S_p{}^\circ$ the standard entropy ($[DX]_{eq}$ = 1.0 mol L^{-1}) of polymerization. However, this equation is valid for high molar mass polymer. For a polymerization system with short linear oligomers being in equilibrium with monomer, an additional term, taking into account the oligomers average chain length (DP_n), has to be introduced (cf. Appendix), and the pertinent equation reads

$$\ln\frac{[DX]_{eq}}{p} = \ln\left(\frac{DP_n}{DP_n - 1}[DX]_{eq}\right) = \frac{\Delta H_p}{RT} - \frac{\Delta S_p{}^\circ}{R} \quad (8)$$

DP_n values of the linear oligomers can be calculated by means of eq 9:

$$DP_n = \frac{[DX]_0 - [DX]_\infty - \sum_{i=2}^{\infty} i[DX(i)]_{eq}}{[BuOH]_0} \quad (9)$$

where $[DX]_{eq}$ and $\sum i[DX(i)]_{eq}$ are the values determined by means of SEC (Figure 3) and MALDI TOF (Table 1), respectively.

Figure 4 shows the plot of $\ln([DX]_{eq}/p)$ vs T^{-1} determined for the bulk polymerization initiated by the Sn-

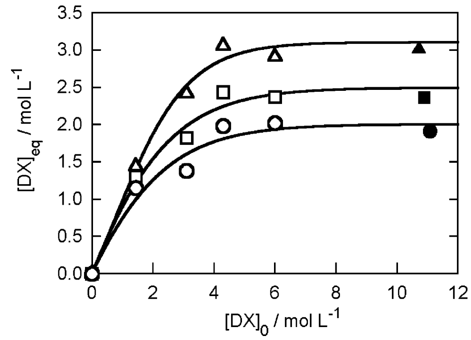


Figure 3. Plots of equilibrium monomer concentrations ($[DX]_{eq}$) on monomer concentration in the feed ($[DX]_0$) as obtained in DX/Sn(Oct)$_2$/BuOH polymerization system. Conditions: $[BuOH]_0$ = 0.058–0.63 mol L^{-1}, $[Sn(Oct)_2]_0 = 10^{-2}$ mol L^{-1}; hollow points, polymerization in 1,4-dioxane solvent; filled points, bulk polymerization; temperature (in °C): 80 (○, ●), 100 (□, ■) and 120 (△, ▲).

Table 1. Effect of $[DX]_0$ and Polymerization Temperature on Cyclic Oligomers Content As Expressed in Molar Concentrations and in Mass Fractions in the Cyclic/Linear Oligomers Mixture[a]

$[DX]_0$/ mol L^{-1}	$[BuOH]_0$/ mol L^{-1}	$\sum_{i=2}^{\infty} i[DX(i)]_{eq}$/mol L^{-1} (mass fraction (f)/%) 80 °C	100 °C	120 °C
1.4	0.058	0.08 (28)	0.03 (21)	≈0
3.1	0.12	0.52 (30)	0.23 (18)	0.12 (17)
4.3	0.15	0.77 (33)	0.77(41)	0.34 (27)
6.0	0.33	0.45 (11)	0.61(17)	0.67 (22)
≈10.9[b]	0.63	0.74 (8)	0.95 (11)	1.20 (16)

[a] DX/Sn(Oct)$_2$/BuOH reacting mixture, 1,4-dioxane as solvent, $[Sn(Oct)_2]_0 = 10^{-2}$ mol L^{-1}. [b] Bulk polymerization.

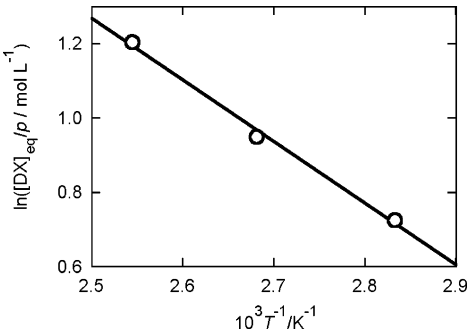
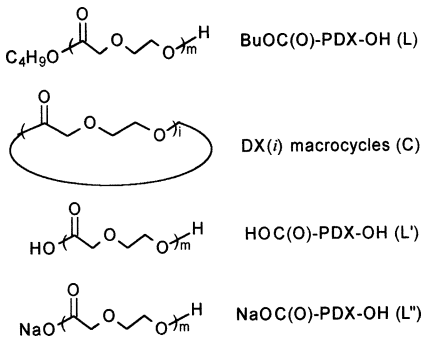


Figure 4. Plot of $\ln([DX]_{eq}/p)$ vs reciprocal of the absolute temperature (T^{-1}) as determined in the bulk polymerization of DX initiated by BuOH/$Sn(Oct)_2$ mixture ($[BuOH]_0 = 0.63$ mol L^{-1}, $[Sn(Oct)_2]_0 = 10^{-2}$ mol L^{-1}).

$(Oct)_2$/BuOH mixture. Using the linear regression (least-squares method) to analyze the experimental data in terms of eq 8, we obtain $\Delta H_p = -(13.8 \pm 0.9)$ kJ mol^{-1} and $\Delta S_p^\circ = -(45.0 \pm 2.5)$ J mol^{-1} K^{-1}. Thus, the determined thermodynamic parameters for DX polymerization are close to those obtained in the polymerizations in which high molar mass PDX was formed: -14.1 kJ mol^{-1} and -45.3 J mol^{-1} K^{-1} (ref 8); -15.8 kJ mol^{-1} and -50.4 J mol^{-1} K^{-1} (ref 9).

(b) Contribution of Cyclic Oligomers. Figure 5 shows a typical MALDI TOF spectrum of PDX prepared in $SnOct_2$/BuOH-initiated polymerization of DX in 1,4-dioxane as solvent. On the basis of this spectrum the following PDX macromolecules have been identified:



Two series of periodically repeating peaks (i.e., being apart of 102.09 *m*/*z*) dominate in the spectrum, namely those corresponding to the linear BuO(O)−PDX−OH chains and to the PDX macrocyclics. Formation of these macromolecules can be explained by a polymerization scheme proposed already in refs 22−25.

The spectrum in Figure 5, given as an instructive example, shows also the presence of short series of signals of lower intensity, corresponding to HOC(O)−PDX−OH (L′) and NaOC(O)−PDX−OH chains. According to our experience, PDX is more prone to undergo hydrolytic degradation, when compared to other aliphatic polyesters, like polylactide or poly(ϵ-caprolactone). Therefore, these species appear, most probably, as products of the PDX hydrolysis during the MALDI TOF measurement, e.g.

$$\text{HO-(dx)}_m\text{-C(O)OBu} + \text{H}_2\text{O} \longrightarrow \text{HO-(dx)}_{m-x}\text{-C(O)OH} + \text{HO-(dx)}_x\text{-C(O)OBu} \quad (10)$$

where dx denotes repeating unit derived from DX monomer; thus $(dx)_m$ stands for PDX.

A similar reaction can take place also for macrocyclic species (DX(*i*)), giving linear HO−$(dx)_i$−C(O)OH chains. It has to be stressed, however, that careful enough PDX work-up during the mass spectra recording (inert gas atmosphere, dried solvents, etc.) allows to avoid the hydrolysis (cf. spectrum in Figure 2) and thus to obtain spectra containing practically only L and C peak series.

The expected M_n of the linear fraction of PDX can be calculated from eq 11:

$$M_n(\text{calcd}) = 102.09([DX]_0 - [DX]_{eq} - \sum i[DX(i)]_{eq})/[BuOH]_0 + 74.12 \quad (11)$$

For the example given by Figure 5—$[DX]_0 = 4.30$ mol L^{-1}, $[BuOH]_0 = 0.15$ mol L^{-1}, $[DX]_{eq} = 2.43$ mol L^{-1}, and $\sum i[DX(i)] = 0.77$ mol L^{-1} (determination of the latter value is described below)—the resulting M_n(calcd) equals 823. This value is very close to that determined for the linear chains fraction in the spectrum given in Figure 5 (M_n(MALDI) = 843).

Further studies of the DX/$SnOct_2$/BuOH system revealed that, depending on the monomer concentration in the feed and the polymerization temperature, the proportion of the linear and cyclic PDX in the resulting

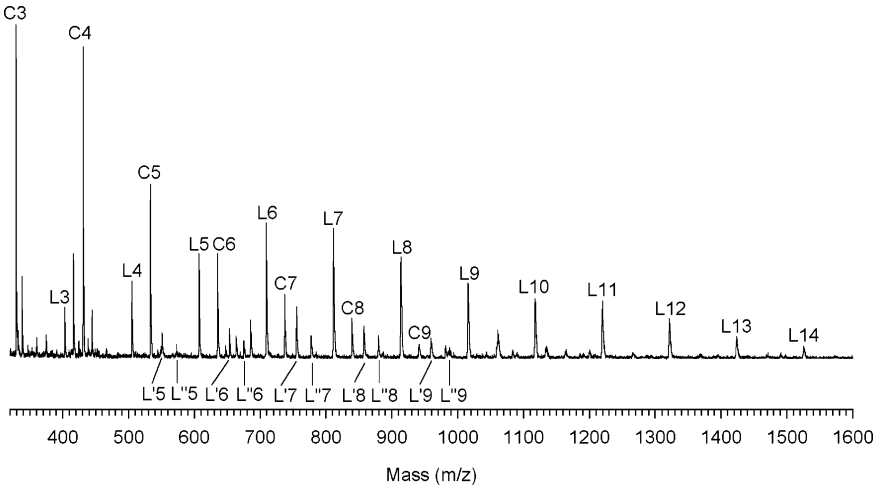


Figure 5. MALDI TOF spectrum of the 1,4-dioxan-2-one/tin octoate/butyl alcohol polymerizing mixture recorded in the linear mode after 24 h from the beginning of polymerization; all marked signals correspond to macromolecules cationized with Na^+, the numbers following L, L′, L″, and C denote degrees of polymerization of the PDX chains and DX(*i*) macrocycles, respectively. Conditions: $[DX]_0 = 4.3$ mol L^{-1}, $[Sn(Oct)_2]_0 = 10^{-2}$ mol L^{-1}, $[BuOH]_0 = 0.15$ mol L^{-1}; 1,4-dioxane solvent, 100 °C.

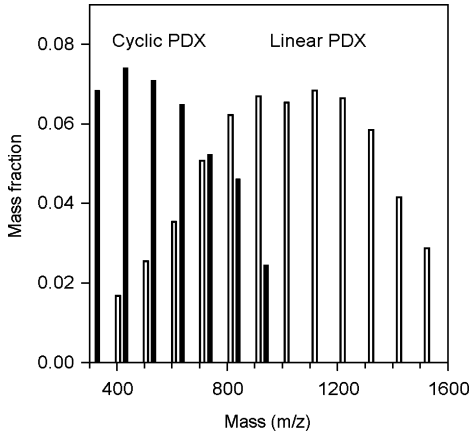


Figure 6. Distribution of mass fractions of the linear (hollow bars) and cyclic (filled bars) PDX macromolecules. Polymerization conditions are given in the caption for Figure 5.

reaction mixtures can differ considerably. Therefore, we decided to describe this phenomenon in a more systematic way.

First, the original MALDI TOF spectra were transformed into the molar mass distribution plots for populations of cyclic and linear macromolecules. This was done by multiplying the intensity of a given signal by polymerization degree of the corresponding L and C species and by dividing by the total sum of thus obtained intensities. Figure 6 shows the corresponding distribution plots, resulting from the spectrum in Figure 5. Signals for the *m*/*z* values above 1600 were too weak to be treated quantitatively.

Eventually, total mass fractions of the linear or cyclic PDX (in terms of the dx repeating units content) have been estimated from the sum of peak intensities corresponding to the individual linear or cyclic species. Analysis of the distribution in Figure 6 gives 41 mass % of macrocyclics (and thus 59 mass % of the linear chains). Taking into account that $[DX]_0 = 4.30$ mol L^{-1} and $[DX]_{eq} = 2.43$ mol L^{-1}, this 41 mass % corresponds to $\sum i[DX(i)]_{eq} = 0.77$ mol L^{-1}.

The MALDI TOF response coefficients are known to depend on end groups and topology (e.g., linear vs cyclics), and this dependence is particularly pronounced at the lower *m*/*z* range (these differences vanish practically above $m/z = 2000$). However, as it has been shown in ref 30, the total differences in responses for macromolecules of various types do not exceed ≈30%. Therefore, in our opinion, it is possible to use the approach described above, but it is necessary to take into account the semiquantitative feature of the MALDI TOF measurements.

Results of similar measurements performed for other compositions of the reacting mixtures and polymerization temperatures are collected in Table 1. These data point out a general tendency—the molar concentration of cyclic oligomers ($\sum i[DX(i)]_{eq}$) increases with increasing monomer concentration in the feed and temperature, at least for $[DX]_0 > 4.3$ mol L^{-1}. $\sum i[DX(i)]_{eq}$ reaches a maximum value equal approximately to 1 mol L^{-1} for polymerization in bulk. From a practical point of view more interesting is the dependence of mass fraction (*f*) of cyclics on polymerization conditions. For lower $[DX]_0$ *f* reaches a value as high as 40% ($[DX]_0 = 4.3$ mol L^{-1}, 100 °C), but after passing a maximum, *f* decreases with increasing $[DX]_0$ and, eventually for the bulk polymerization, falls down below 10% (for example $f = 8\%$ at 80 °C). This is, however, still a high value and in order to depress stronger the cyclic oligomers content in DX polymerization the kinetic control is required. Studies of the latter problem are in progress in our laboratories.

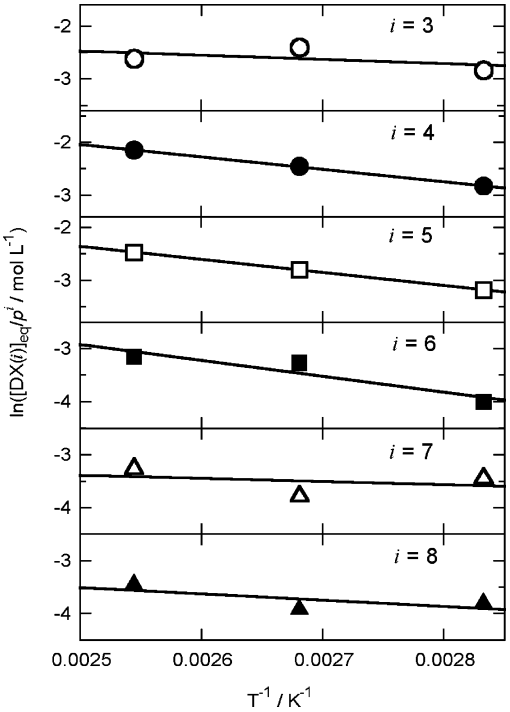


Figure 7. Plots of $\ln([DX(i)]_{eq}/p^i)$ vs reciprocal of the absolute temperature (T^{-1}) for a bulk polymerization of DX initiated by BuOH/Sn(Oct)$_2$ mixture ($[BuOH]_0 = 0.63$ mol L^{-1}, $[Sn(Oct)_2]_0 = 10^{-2}$ mol L^{-1}).

(c) Temperature Dependence of Cyclic Oligomers Fraction. Results presented in Table 1 show that $\sum i[DX(i)]_{eq}$ depends both on $[DX]_0$ and on the polymerization temperature. Therefore, to make further discussion more clear, an analysis of the temperature dependencies of $[DX(i)]_{eq}$ will be limited to the bulk polymerization.

The equilibrium constant of propagation for the individual macrocycle DX(*i*), being in equilibrium with linear oligomers, can be expressed in terms of its equilibrium concentration ($[DX(i)]_{eq}$) as

$$K_{pi} = \frac{1}{[DX(i)]_{eq}} p^i \qquad (12)$$

(cf. eqs 5 and 6 and eq 15 in the Appendix). Thus, the expression for the temperature dependence of $[DX(i)]_{eq}$ reads

$$\ln \frac{[DX(i)]_{eq}}{p^i} = \frac{\Delta H_p(i)}{RT} - \frac{\Delta S_p^\circ(i)}{R} \qquad (13)$$

Figure 7 shows the plot of $\ln([DX(i)]_{eq}/p^i)$ vs T^{-1} obtained for the bulk polymerization initiated by Sn(Oct)$_2$/BuOH mixture. $[DX(i)]_{eq}$ has been determined on the basis of the total concentration of the macrocyclic fraction ($\sum i[DX(i)]_{eq}$, Table 1) and from the relative intensities of the signals in the MALDI TOF spectrum corresponding to the individual cyclic oligomer DX(*i*). The parameter *p* has been calculated as described in the above section: (a) equilibrium monomer concentration as a function of $[DX]_0$. The resulting thermodynamic parameters of DX(*i*) propagation are collected in Table 2.

Table 2. Enthalpies ($\Delta H_p(i)$) and Entropies ($\Delta S_p°(i)$) of Propagation of Cyclic Oligomers (DX(i)) Formed in DX Bulk Polymerization[a]

i in DX(i)	$\Delta H_p(i)$/kJ mol^{-1}	$\Delta S_p°(i)$/J mol^{-1} K^{-1}
1	-13.8 ± 0.9	-45.0 ± 2.5
2		
3	-7 ± 11	4 ± 28
4	-19.6 ± 0.5	-32 ± 1
5	-20.4 ± 0.3	-31.4 ± 0.9
6	-25 ± 10	-38 ± 26
7	-5 ± 15	16 ± 39
8	-10 ± 10	4 ± 27

[a] Polymerization conditions given in the caption for Figure 7.

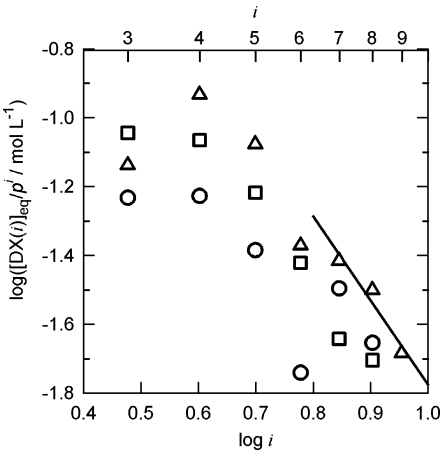


Figure 8. Bilogarthmic dependence of molar cyclization equilibrium constants ($K_{di} = 1/K_{pi} = [DX(i)]_{eq}/p^i$) on the number of dx repeating units in DX(i) macrocycle for a bulk polymerization of DX initiated by BuOH/Sn(Oct)$_2$ mixture. Conditions: $[BuOH]_0 = 0.63$ mol L^{-1}, $[Sn(Oct)_2]_0 = 10^{-2}$ mol L^{-1}; temperature (in °C): 80 (○), 100 (□), and 120 (△).

Temperature dependencies of cyclic oligomers concentration in the ring-opening polymerization of cyclic esters have not been studied systematically. Results of the preliminary measurements performed by Ito and Yamashita[31] in the anionic polymerization of ϵ-caprolactone in THF as solvent have shown that concentration of cyclic CL(i) oligomers changed very little in the temperature range from −78 to 50 °C. This observation allowed to conclude that $\Delta H_p(i) \approx 0$ (where $i \geq 2$). Also, for other polymerizing systems, in which ring−chain equilibria take place, it is generally accepted that propagation (or depropagation) of larger cyclics is accompanied by the enthalpy changes equal to zero.[32]

Although quantitative data on DX(i) concentration obtained in the present work have to be taken with a reserve, because of a limited accuracy of the MALDI TOF measurements, certain conclusions on their basis can be drawn. First, DX dimer (DX(2)) could hardly be detected in the crude reacting mixtures, and the pertinent peak was practically absent in the majority of the analyzed mass spectrograms. Probably, this can be ascribed to the large ring strain of DX(2). It is interesting to note that tetramer, pentamer, and hexamer exhibit a relatively large ring strain, being close to that of the monomer, which may result from the transannular interactions. On the other hand, trimer, heptamer, and octamer are almost strainless within the calculated experimental error.

Moreover, the gradient in the plot of log K_{di} against log i for $i = 7$, 8, and 9, determined in a bulk polymerization of DX conducted at 120 °C (Figure 8, triangles), is equal to −2.4. Thus, it is not far from −2.5, the value

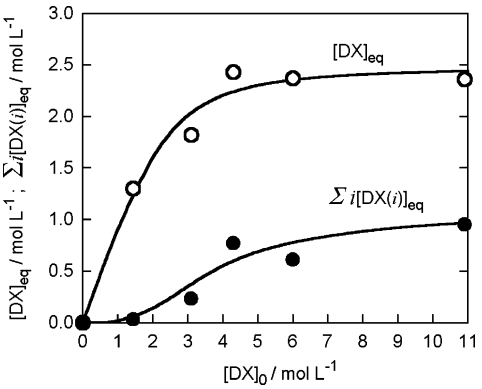


Figure 9. Comparison of experimental and computed (eqs 19−21) dependencies of $[DX]_{eq}$ and $\Sigma i[DX(i)]_{eq}$ on $[DX]_0$. Points, experimental; lines, computed using numerical curve fitting to the experimental data. Polymerization conditions: $[BuOH]_0 = 0.058-0.63$ mol L^{-1}, $[Sn(Oct)_2]_0 = 10^{-2}$ mol L^{-1}; 1,4-dioxane as solvent, 100 °C.

characteristic for the strainless macrocycles, as predicted by the Jacobson−Stockmayer theory (eq 14).

$$K_{di} = 1/K_{pi} = Ai^{-2.5} \qquad (14)$$

On the basis of general equation, derived in the Appendix (eq 18), relating $[DX]_0$, $[DX]_{eq}$, $[DX(i)]_{eq}$, and $[dx]_{linear}$, it is possible to compute dependencies of $[DX]_{eq}$ and/or $\Sigma i[DX(i)]_{eq}$ on $[DX]_0$ and to estimate the equilibrium constants of the propagation of the cyclic species (K_{pi}) by numerical curve fitting to the experimental data.

Figure 9 shows a result of such analysis performed for polymerization in the DX/Sn(Oct)$_2$/BuOH system at 100 °C. Curves drawn in Figure 9 have been computed using eqs 16−18 and assuming $K_{p1} = 0.38$ mol^{-1} L, $1/K_{p2} = 0$, and for $i \geq 3$ $K_{pi} = A^{-1}i^{5/2}$ where $A = 1.87$ mol L^{-1}. The latter values were obtained by numerical curve fitting using Matlab version 6.5 (MathWorks Inc.) computer program. Indeed, in the majority of spectra a cyclic dimer was not observed or its intensity was well below the values observed for the next cyclics in series (trimer, tetramer, etc.). In the first approximation, it was assumed also that all macrocycles, starting from trimer, conform to a Jacobson−Stockmayer relationship (eq 14), i.e., that they are strainless. Although there is a certain scatter of the experimental points (related to the accuracy of SEC and MALDI TOF measurements), the agreement between experimental and computed dependencies is satisfactory.

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Appendix

In the case of ring−chain equilibria presented sche-

matically in eq 5, the following relationship holds:[34]

$$[\mathrm{DX}(i)]_{\mathrm{eq}} = \frac{1}{K_{\mathrm{p}i}} \frac{[\mathrm{dx}(k+i)]}{[\mathrm{dx}(k)]} = \frac{1}{K_{\mathrm{p}i}} \left(\frac{[\mathrm{dx}(k+1)]}{[\mathrm{dx}(k)]} \right)^i = \frac{1}{K_{\mathrm{p}i}} p^i \tag{15}$$

where $[\mathrm{DX}(i)]_{\mathrm{eq}}$ and $[\mathrm{dx}(k)]$ denote equilibrium concentrations of a cyclic i-mer and a linear k-mer, respectively, $K_{\mathrm{p}i}$ is the equilibrium constant of propagation ⇌ depropagation of a cyclic i-mer, and $p = [\mathrm{dx}(k+1)]/[\mathrm{dx}(k)]$ (on the other hand, $p = (\mathrm{DP_n} - 1)/\mathrm{DP_n}$).[34]

For $i \geq i_{\min}$ (where $i_{\min}$ is a minimal size of cycles conforming to the Jacobson−Stockmayer relationship), $1/K_{\mathrm{p}i} = Ai^{-5/2}$ (eq 14). Thus, concentration of repeating units in a cyclic fraction (including monomer) reads

$$[\mathrm{dx}]_{\mathrm{cycl}} = \sum_{i=1}^{\infty} i[\mathrm{DX}(i)] = \sum_{i=1}^{\infty} i \frac{p^i}{K_{\mathrm{p}i}} = \sum_{i=1}^{i_{\min}-1} i \frac{p^i}{K_{\mathrm{p}i}} + A \sum_{i=i_{\min}}^{\infty} i^{-3/2} p^i \tag{16}$$

Whereas the concentration of repeating units in a linear polymer fraction is

$$[\mathrm{dx}]_{\mathrm{linear}} = \sum_{i=1}^{\infty} i[\mathrm{dx}(i)] = \sum_{i=1}^{\infty} i[\mathrm{dx}(1)]p^{i-1} = \frac{[\mathrm{dx}(1)]}{(1-p)^2} = \frac{[\mathrm{L}]}{1-p} = \frac{[\mathrm{BuOH}]_0}{1-p} \tag{17}$$

where [L] denotes concentration of linear chains, equal in the present system to the starting concentration of BuOH.

Combination of eqs 16 and 17 yields an equation with one unknown (p):

$$[\mathrm{DX}]_0 = [\mathrm{DX}]_{\mathrm{eq}} + \sum_{i=2}^{i_{\min}-1} i \frac{p^i}{K_{\mathrm{p}i}} + A \sum_{i=i_{\min}}^{\infty} i^{-3/2} p^i + \frac{[\mathrm{BuOH}]_0}{1-p} \tag{18}$$

where DX stands for DX(1) and $[\mathrm{DX}]_{\mathrm{eq}} = p/K_{\mathrm{p}1}$. A function $F(p) = \sum i^{-3/2} p^i$ can be determined numerically.

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