2,2-Di-n-butyl-1,3,2-dioxastannolane/Di-n-butyltin Dichloride: an Excellent Catalytic System for Cyclo-oligomerization of Lactones

Stefano Roelens

C.N.R. Centro di Studio sulla Chimica e la Struttura dei Composti Eterociclici e loro Applicazioni, c/o Department of Organic Chemistry, via Gino Capponi 9, 50121 Firenze, Italy

The catalytic system 2,2-di-n-butyl-1,3,2-dioxastannolane/di-n-butyltin dichloride (DOS/DTC) induces clean cyclo-oligomerization of β-propiolactone and ε-caprolactone to an equilibrium distribution of oligolactones in dilute solution under unusually mild conditions.

In most polymerizations of lactones, variable amounts of cyclic oligomers are obtained, either during direct polymerization or in the depolymerization processes.[1] Their abundance relative to the polymer is strongly dependent not only on reaction conditions but also on the specific catalyst. Furthermore, the distribution of cyclics is kinetically controlled[2] or, more often, more or less extensively equilibrated, as in pyrolytic depolymerizations.[3] Clean thermodynamic distributions, however, are hardly achieved because of degradation of material under the quite severe conditions usually required for equilibration, and are often difficult to establish[4] because of lack of suitable 'equilibrium' standards. Equilibrated distributions are essential to obtain the molar cyclization equilibrium constants, which have been evaluated in some cases[5] and used to test the validity of the Jacobson–Stockmayer cyclization theory[6] describing equilibrated mixtures of polymers.

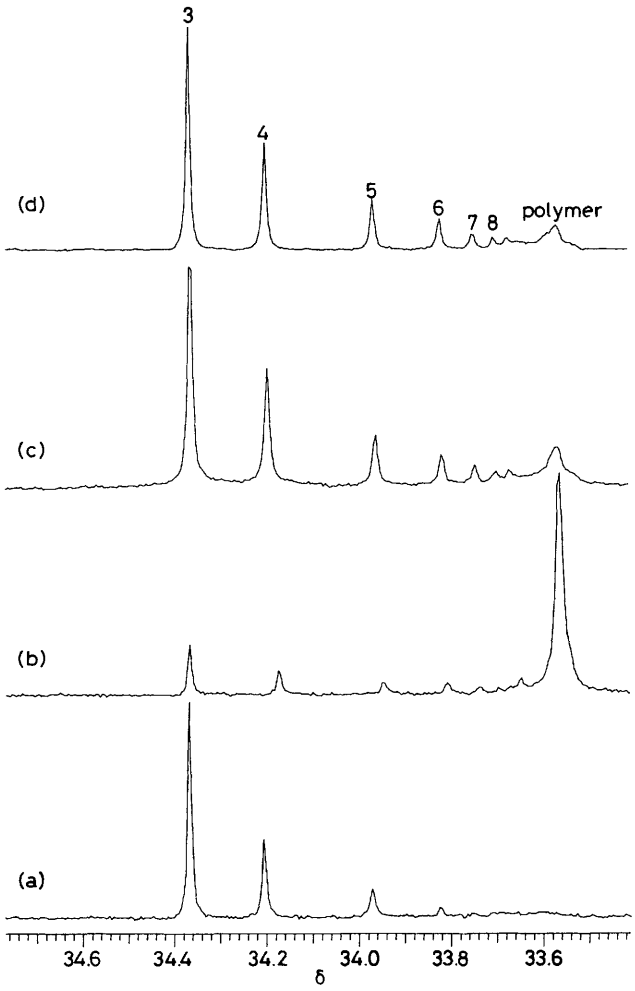


Figure 1. ^{13}C NMR spectra of equilibrium distributions of $(OCH_2CH_2CO)_n$, oligomerized in $CDCl_3$ in the presence of DOS/DTC, at (a) 0.1 M initial monomer concentration, (b) 4.0 M initial monomer concentration, (c) solution of (b) re-equilibrated at 0.51 M, (d) 0.51 M initial monomer concentration, detected by the signals of the carbon next to the carbonyl group. The number on each peak indicates the degree of polymerization of the corresponding cyclic oligomer. (a) $n = 3$, 53%; $n = 4$, 21%; $n = 5$, 10%; $n = 6$, 3%; $n = 7$, 1%; $n > 7$ + polymer, 12%; (b) $n = 3$, 8%; $n = 4$, 4%; $n = 5$, 3%; $n = 6$, 2%; $n = 7$, 1%; $n > 7$ + polymer, 82%; (c) $n = 3$, 37%; $n = 4$, 20%; $n = 5$, 9%; $n = 6$, 6%; $n = 7$, 3%; $n = 8$, 2%; $n > 8$ + polymer, 23%; (d) $n = 3$, 37%; $n = 4$, 20%; $n = 5$, 10%; $n = 6$, 6%; $n = 7$, 3%; $n = 8$, 2%; $n > 8$ + polymer, 22%. Data (as mole % of monomer) are evaluated by integration of spectra acquired under appropriate conditions (30° pulse angle and a cycle time of 5.6 s, with T_1 values measured to range from 1.1 s for the trimer to 0.4 s for the polymer signal).

Recently, organotin oxides and carboxylates have been widely used in the polymerization of esters and lactones because of their high catalytic activity.[7] In the course of our investigation on the monoesterification of diols,[8] it has been shown that 2,2-di-n-butyl-1,3,2-dioxastannolane (DOS), when in the presence of di-n-butyltin dichloride (DTC), acts as a very efficient transesterification catalytic system (indicated as DOS/DTC),† which was found to be responsible for the fast equilibration of cyclic oligoethylene diglycolates[9] and other alicyclic dicarboxylates.[10]

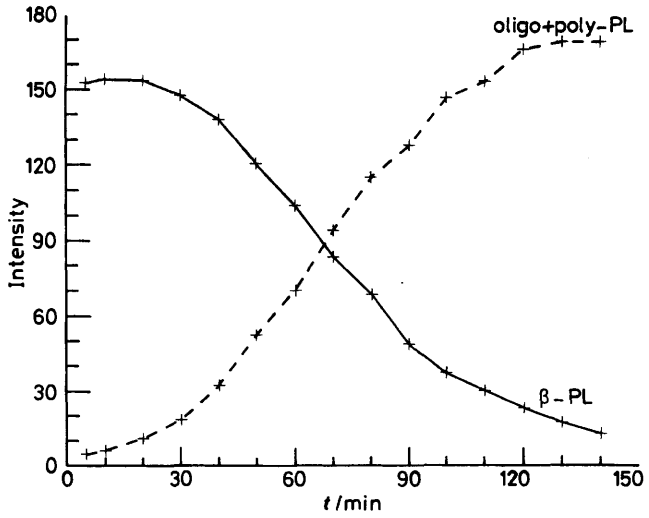


Figure 2. Kinetics of oligomerization of (1) (β-PL) 0.6 M in $CDCl_3$ at 333 K, in the presence of DOS/DTC (0.03 M), monitored by the intensity (reported in an arbitrary scale) of the ^1H NMR signals of the methylene next to the carbonyl group at δ 3.54 (β-PL) and δ 2.56—2.78 (oligo- and poly-PL).

† The nature of the DOS/DTC adduct has been described in detail in ref. 8.

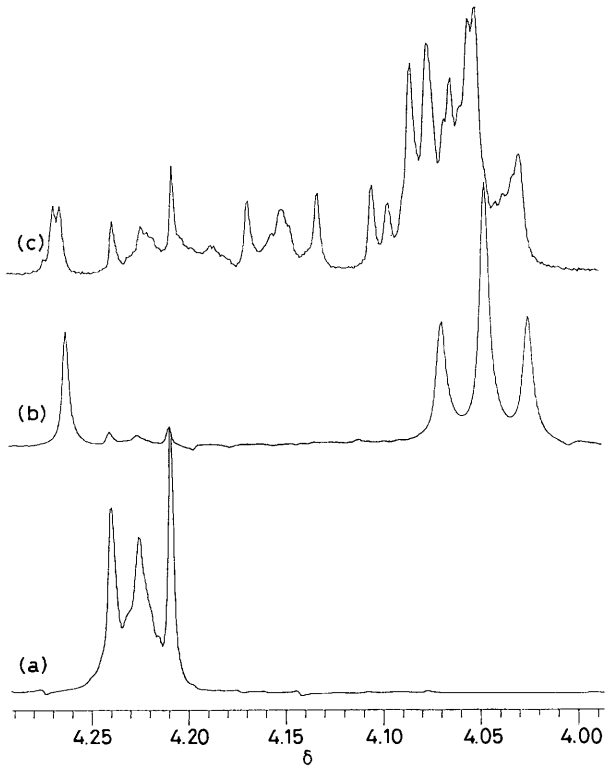
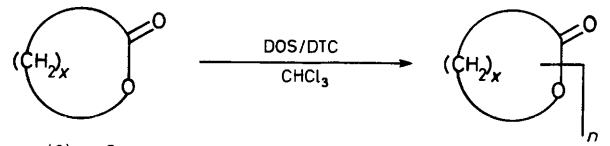


Figure 3. ^{1}H NMR spectra of ε-caprolactone (1.1 M) in $CDCl_3$ (a) unaltered after 29 h at 293 K in the presence of DOS (0.3 M); (b) oligomerized for 30 h at 293 K in the presence of DOS/DTC (0.2 M); (c) re-equilibrated for 36 h at 336 K after a ten-fold dilution. Only the spectral region of the CH_2O signals is reported.



(1) $x=2$
(2) $x=5$

Scheme 1

The present communication reports that DOS/DTC can be used as a new and particularly convenient catalytic system for the oligomerization of lactones (Scheme 1).

β-Propiolactone [(**1**), 0.1 M in chloroform] has been oligomerized at 333 K in the presence of DOS/DTC in 1 : 1 ratio (0.03 M) and the resulting distribution is reported in Figure 1(a).‡ Except for a small amount of products bearing stannylated terminals (5% mol. *ca.*, detected by ^{1}H NMR spectroscopic analysis of CH_2OSn end groups) only cyclic oligomeric esters were detected, with little occurrence of higher oligomers and polymer. A blank experiment under the same conditions, in the absence of DOS/DTC, showed no trace of oligomerization after 26 h at 343 K.

To prove that truly equilibrated distributions are achieved, a mixture obtained from a concentrated solution of (**1**) [4.0 M, Figure 1(b)] has been diluted to 0.51 M, re-equilibrated in the presence of 10% mol of DOS/DTC, and the resulting distribution [Figure 1(c)] compared with that obtained from a reaction run at 0.51 M initial concentration [Figure 1(d)]. The intensities in the reported spectra gave identical distributions for the two mixtures. Preliminary kinetic experiments on the oligomerization of (**1**) in the presence of DOS/DTC at various concentrations of both (a typical case is reported in Figure 2), showed that the reaction mixture is free from degradation products and that, after an induction period dependent on the concentration of DOS/DTC, is quite fast, even at 333 K and low concentration of reagent and catalyst.

ε-Caprolactone [(**2**), 1.1 M, DOS/DTC 0.2 M in chloroform], unaltered after 29 h in the presence of 0.3 M DOS alone [Figure 3(a)], disappeared in a few hours at room temperature (293 K), showing nearly complete polymerization to higher oligomers after 30 h [Figure 3(b)], but the mixture re-equilibrated upon a ten-fold dilution to give cyclic oligomers in 36 h at 336 K [Figure 3(c)], after which no further redistribution was observed.§

Experimental results reveal that this is indeed a unique catalytic system for generating cleanly a living ring–chain equilibrium of oligolactones, in short reaction times even in dilute solution, and under conditions which are unusually mild for equilibration reactions.

Some remarkable features of DOS/DTC are, firstly, unlike other active catalysts,[11,12] it is an easy to handle solid, not particularly sensitive to air or moisture, and can be generated *in situ* from commercial reagents without further purification;¶ secondly, it is a neutral and highly soluble catalyst, that affords product mixtures essentially devoid of by-products; ‖ thirdly, because of its high activity in dilute solutions, it is ideal for promoting cyclo-oligomerization reactions and for the experimental determination of equilibrium parameters; and fourthly, its efficiency towards lactones appears to be comparable to or greater than that of highly active and more strongly basic alkyltin methoxides,[7] but far larger than DOS alone, which gives unreliable results.**

‡ Oligolactones of (**1**) have been fully characterized.[12] In the present work, identification of cyclic oligomers has been done by combined ^{13}C NMR and FAB mass spectrometry. In agreement with the above authors, the trimer is the first and most abundant observed oligomer of the distribution. This has been proved by the FAB MS spiked with CsI, in which the lack of the $M + 133$ peaks corresponding to the monomer and the dimer showed unambiguously that they were actually due to fragmentation of higher oligomers. *Selected spectroscopic data:* (CH_2CO, ^{13}C NMR, 75 MHz, $CDCl_3$ internal secondary reference at δ 77.00, data relative to the untreated reaction mixture at the same concentration; positive FAB MS, Xe, 6 kV, glycerol), $n = 3$, δ 34.371, *m/z* 217 ($M + 1$); $n = 4$, δ 34.210, *m/z* 289 ($M + 1$); $n = 5$, δ 33.977, *m/z* 361 ($M + 1$); $n = 6$, δ 33.831, *m/z* 433 ($M + 1$); $n = 7$, δ 33.758, *m/z* 505 ($M + 1$); $n = 8$, δ 33.712, *m/z* 577 ($M + 1$).

§ The observed behaviour is essentially identical to that described by K. Ito *et al.*[11] which reported a living ring-chain equilibrium system for ε-caprolactone under the action of a different catalyst [K-t-butoxide/tetrahydrofuran(THF)]. Oligolactones have been fully characterized by the above authors. In the present work, identification of cyclic oligomers has been done by combined ^{13}C NMR and FAB MS. *Selected spectroscopic data:* (CH_2CO, ^{13}C NMR, 75 MHz, $CDCl_3$ internal secondary reference at δ 77.00, data relative to the untreated reaction mixture at the same concentration; positive FAB MS, Xe, 6 kV, 1-thioglycerol), $n = 1$, δ 34.541, *m/z* 115 ($M + 1$); $n = 2$, δ 34.237, *m/z* 229 ($M + 1$); $n = 3$, δ 34.202, *m/z* 343 ($M + 1$); $n = 4$, δ 34.169, *m/z* 457 ($M + 1$); $n = 5$, δ 34.148, *m/z* 571 ($M + 1$); $n = 6$, δ 34.135, *m/z* 685 ($M + 1$); $n = 7$, δ 34.122, *m/z* 799 ($M + 1$); $n = 8$, *m/z* 913 ($M + 1$); $n = 9$, *m/z* 1027 ($M + 1$); $n = 10$, *m/z* 1141 ($M + 1$).

¶ For the preparation of DOS from ethylene glycol, see: W. J. Considine, *J. Organomet. Chem.*, 1966, **5**, 263.

‖ By-products are formed with active catalysts, typically in the case of β-propiolactone.[12]

** Although DOS has been used to oligomerize β-propiolactone (A. Shanzer, J. Libman, and F. Frolow, *J. Am. Chem. Soc.*, 1981, **103**, 7339) in our hands as well as in others' (D. Seebach, U. Brändli, P. Schnurrenberger, and M. Przybylski, *Helv. Chim. Acta*, 1988, **71**, 158) it failed to give cyclic oligomers.

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