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WHAT WE HAVE LEARNED IN GENERAL FROM CYCLIC ESTERS POLYMERIZATION

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SUMMARY: The major general phenomena observed in the ionic and covalent – coordinated polymerization of cyclic esters are reviewed. Reactivities of ions, mechanisms of propagation on metal alkoxides and carboxylates are analysed on the basis of results from the authors' laboratory.

Introduction

There are three major reasons for studying polymerization of cyclic esters. First: to find the "best" conditions for the technological process. The expression "best" is encompassing a number of aspects, including economy, ecology and technical features. Second: to prepare various macromolecular models, including well defined structures, desired stereochemistry and end-groups for homopolymers as well as defined grafts, blocks, stars etc. These are further used for studies of their physical properties. Finally, cyclic esters are versatile models for studying the kinetics, thermodynamics, and mechanisms of elementary reactions in polymerization. Some of the established phenomena are more general and are not merely related to the polymerization of cyclic esters. This lecture will mostly discuss these general phenomena that became understood on the basis of our studies of cyclic esters polymerization, comprising ionic and covalent (pseudoionic) propagation. In anionic polymerization an interesting new fact was related to the inversion of reactivities of ions and ion pairs (Slomkowski & Penczek, 1980[1)]) and enhanced selectivity when cryptated (Boileau, 1976[2)]) or crowned active species were applied (Slomkowski & Penczek, 1976[3)]). In the pseudoionic processes the influence on the polymerization kinetics of the coexistence of various aggregated forms of initiators (Duda & Penczek, 1995[4,5)]), and propagating species (with slow and fast interconversion) has been established (Duda & Penczek; 1991[6)]). The corresponding findings contribute to the long lasting general discussion on the reactivities of aggregated species in ionic polymerization. The novel methods of kinetic analysis elaborated

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in our group allow simultaneous determination of both aggregation and rate constants and give access to these constants in the similar kinetic instances (Szymanski, Duda, Penczek, 1991-1998$^{6-9)}$). Finally, experimental conditions have been found allowing determination of the rate constants of bimolecular transfer (k_{tr2}) from one macromolecule to another, (i.e. segmental exchange) (same authors, 1997$^{10-13)}$). On this basis it was possible to correlate the selectivity of polymerization on a given active species to its structure. This has been done for a number (still increasing) of active species: ...-$O^{\ominus}$, $Mt^{\oplus}$; $Sm(OR)_3$; $La(OR)_3$; $Ti(OR)_4$; $Fe(OR)_3$; $Al(OR)_3$; $Sn(OR)_2$ (selectivity grows in this order). Under investigation is a general problem of interconversion of the covalent metal carboxylates and metal alkoxides, explaining, that e.g. $Sn(Oct)_2$ does not initiate polymerization by itself (at least of ϵ-caprolactone and lactides) and has to be converted into the corresponding Sn^{II}-alkoxide in order to initiate polymerization. This is probably a general phenomenon, that applies also to other metal carboxylates.

Therefore studies of polymerization of cyclic esters for one side provide either new materials or improved polymerization processes and for the other allow studying more general problems, general for all of the polymer chemistry and beyond. This field has become particularly interesting since polycaprolactone and polylactide are transformed into industrial realities.

One of us has recently been invited to visited the polylactide plant of Cargill (USA) and understood better how essential questions have still to be solved before polylactide at 50¢/pound will become a commodity plastic and not merely the biomedical product. Basic research is still needed to answer questions asked by technology.

Ionic Polymerization of Cyclic Esters

The quantitative studies of elementary reactions in the polymerization of cyclic esters, that are the main subject of this paper, were started by converting or "upgrading" polymerization of β-propiolactone βPL from nonliving to the living conditions. This happened over twenty years ago when two papers appeared in the same issue of *Macromolecules* in 1976, namely our paper on application of crown ethers$^{3)}$ and paper of S. Boileau on cryptates$^{2)}$. Both papers, published in this order, revealed the same phenomenon, the large increase of the observed rate of polymerization and depression of transfers with these complexing agents.

This increase of rate of polymerization when initiated with crowned potassium acetate was over 10^2 times. In agreement with what has already been known at that time on the influence of crown ethers and cryptates on the behaviour of ionic reactions it was assumed, that cryptates brake down the aggregates of ion-pairs, converting the unreactive aggregates into the unimeric ion-pairs with cryptated cations. The next consequence was the increase of concentration of the so-called free ions, due to the much higher dissociation constant of the crowned ion pairs. Polymerization was internally first order in monomer and the apparent rate constant was proportional to the determined independently degree of ionization (α). Besides, molar masses were linear functions of conversion up to $M_n = 2 \cdot 10^4$. These results are illustrated in Fig. 1 taken from our paper3).

Later on, Slomkowski was able to go first up to $M_n = 1.5 \cdot 10^5$ in a controlled way14(a)) and eventually prepared polymers14 (b) with M_n up to $\approx 5 \cdot 10^5$, which seems to be a limit, at least at room temperature, set by the chain transfer on monomer. The k_p/k_{tr} for βPL was later estimated by Duda as equal to 10^4, at least one hundred times larger than for the methyl β-substitued βPL (i. e β-butyrolactone)15). On this basis it was possible to move further on and study the actual propagation process. This system was of particular interest, since a few papers from the Paris group (Boileau and Hemery16,17)) reported that some ion pairs are more reactive than ions, similar result was indicated for a substituted lactone. Push-pull mechanism was adopted for cyclic sulfides and a particular steric interaction for the substituted lactone.

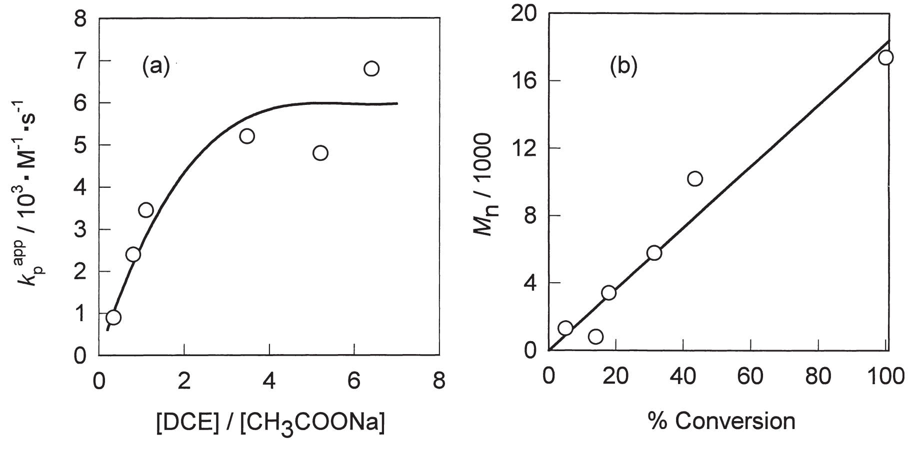


Fig. 1: (a) Dependence of the apparent rate constant of propagation (k_p^{app}) on the [DCE]/[$CH_3C(O)ONa$]$_0$ ratio for the polymerization of βPL in CH_2Cl_2 at 35°C: [βPL]$_0$ = 3 mol·L^{-1}, [$CH_3C(O)ONa$]$_0$ = $3.8 \cdot 10^{-3}$ mol·L^{-1}. (b) Dependence of M_n of poly(βPL) on conversion in the polymerization of βPL in CH_2Cl_2 at 35°C: [βPL]$_0$ = 2.32 mol·L^{-1}, [$CH_3C(O)ONa$]$_0$ = $7.79 \cdot 10^{-3}$ mol·L^{-1}, [DCE] = $1.48 \cdot 10^{-2}$ mol·L^{-1} (where DCE denotes dibenzo-18-crown-6 ether). (Reprinted with permission from Ref. 3. Copyright 1981 American Chemical Society).

In our work we determined the contribiution of ions and ion pairs at various temperatures. The dissociation degrees (α) were calculated from the dissociation constants (K_D) determined by conductivity measurements. These K_D's were found to be practically independent on temperature. Thus, $K_D = 5.6 \cdot 10^{-6}$ mol·L^{-1} at $[\beta PL]_0 = 1$ mol·L^{-1} and $K_D = 5.0 \cdot 10^{-5}$ mol·L^{-1} at $[\beta PL]_0 = 3.0$ mol·L^{-1} (CH_2Cl_2 solvent). The resulting values of K_D mean that the proportion of ions vary from a few percent to almost 20% in these studies. Dependence of the apparent rate constants of propagation (k_p^{app}) on dissociation degree (α) is presented in Fig. 2.

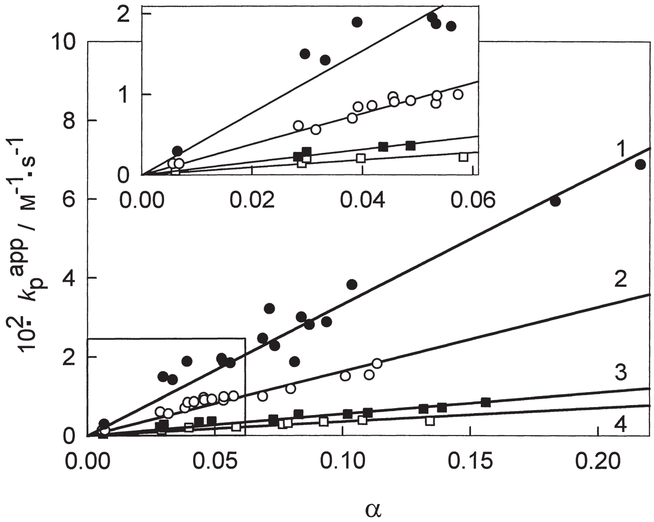


Fig. 2: Dependence of the apparent rate constants of propagation (k_p^{app}) on the dissociation degree (α) for $[\beta PL]_0 = 3$ mol·L^{-1}, initiator $CH_3C(O)OK$/DCE, CH_2Cl_2 solvent: (1) 35°C, (2) 25°C, (3) 15°C, (4) 10°C. Points for α lower then 0.01 correspond to experiments with addition of $Ph_4B^-K^+$ DCE. (Reprinted with permission from Ref. 3. Copyright 1981 American Chemical Society).

Results of these measurements have lead to the observation of an unexpected and general phenomenon, unknown till that time, (i.e. 1980), in the field of cyclic esters polymerization. It is illustrated in Fig. 3. showing the dependence of the rate constants of propagation on ions and ion pairs as the function of temperature and at two different concentrations of βPL and in two different solvents. βPL is a highly polar component able to solvate both cations and anions. Kinetically, the ion pairs show a "normal" behaviour. At both 1.0 and 3.0 mol·L^{-1} of βPL their reactivity is the same, meaning, that the crowned ion pairs are not specifically solvated by components of the system. This is because ion pairs are electrically neutral and their cation is not easily accessible, due to its crowned character. At higher concentration of βPL the reactivity of ions becomes lower than at low βPL concentration. On the other hand, at low temperature the reactivity of ions approaches the reactivity of ion pairs. In DMF solvent for the same monomer at 1.0 mol·L^{-1} the same phenomena were observed by Slomkowski[14(a)]. Here it was possible to reach a temperature, at which there is an observable inversion of reactivities of ions and ion pairs. Apparently at this low temperature the solvation of ions is so strong, that additional energy is required to remove solvent molecules from its immediate sourroundings, making ions relatively less reactive.

Similar phenomena were also observed for the polymerization of ε-caprolactone[18)]. Reactivities of both ions and ion pairs came close one to another but inversion could only be expected by extrapolation although not directly observed. When polymerization of ε-caprolactone (εCL) without crown ether was used then K_D is so low ($4.2 \cdot 10^{-10}$ mol·L^{-1} at 25°C in THF), that ions practically do not participate in the chain growth and the external order in initiator being slightly higher than 1[19)].

Thus, inversion of reactivities of ions and ion pairs first observed in these works is posing a question: what are the conditions needed to have either ions or ion pairs more reactive. This is a general question and important one, since selectivities in reactions with ions and ion pairs may differ.

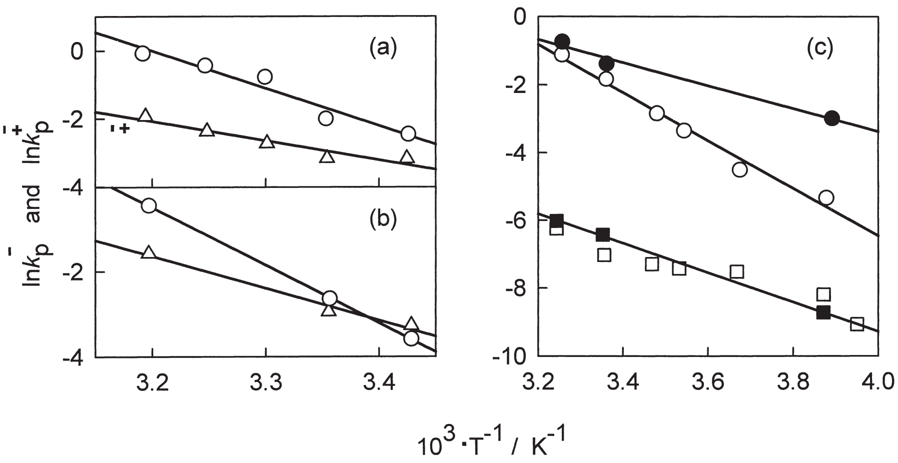


Fig. 3: Semilogarithmic dependencies of the rate constants of propagation on ions (k_p^-) and ion pairs ($k_p^{\pm}$) versus reciprocal of the absolute temperature in the polymerization of βPL. (a) k_p^-(o), $k_p^{\pm}$ (Δ), $[\beta PL]_0 = 5 \cdot 10^{-1}$ mol·L^{-1} in DMF, (b) k_p^-(○), $k_p^{\pm}$ (Δ); $[\beta PL]_0 = 1$ mol·L^{-1} in DMF, (c) k_p^- (●) $[\beta PL]_0 = 1$ mol·L^{-1}, k_p^- (○) $[\beta PL]_0 = 3$ mol·L^{-}]and $k_p^{\pm}$ (■) $[\beta PL]_0 = 1$ mol·L^{-1}; $k_p^{\pm}$ (□), $[\beta PL]_0 = 3$ mol·L^{-1}) in CH_2Cl_2 (Reproduced with permission from Ref. 14 (a) (Fig. (a) and (b)), and from Ref. 1 (Fig. (c)). Copyright 1986 Elsevier and 1980 American Chemical Society, respectively).

Therefore, we may be interested in shifting from one species to another by carefully choosing the reaction conditions, namely solvation by using the solvating components and changing accordingly the temperature.

This inversion may be explained by the nonspecific (ion-pairs) and specific (ions) solvation.

Ion pair ion

Thus, we assume that around the macroion pair (~~~⊖, ⊕) solvent (S) and monomer (M) molecules are packed disorderly in the available space and being not oriented in any specific way. On the contrary, macroion is specifically solvated, and the thermodynamic potential of the monomer molecules solvating the active species differ from this of monomer in solution. The lower the temperature the more perfect becomes the solvation shell around ions and removal of solvent and/or monomer molecules a necessery step preceding propagation, becomes more and more difficult. Thus, the activity of ions decreases faster with lowering temperature than the reactivity of ion pairs, where the solvation is not important and eventually the reactivities become the same followed eventually by inversion of reactivities20).

Aggregation of Active Species

Whenever polar species are present in the system they form various aggregated forms that may differ in reactivity. This may affect initiation if initiators exist in various aggregated forms and are initiating with different rate constants. This is the case of several metal alkoxides. We described this phenomenon for aluminium isopropoxide4,5,9) and we will not discuss these problems here.

Aggregation in propagation has a long and quite colourful history, particularly for lithium alkyls (see, e.g. Refs. 21-23). In the polymerization of cyclic esters we observed aggregation of active species first when we studied polymerization of εCL with sodium trimethylsilanolate24) and then with dialkylaluminium alkoxides6). The direct diagnostics of aggregation comes from kinetics; namely from the external order in initiator. Indeed, if aggregates are not reactive, then we have:

$$P_i^* \quad + \quad M \xrightarrow{k_p} P_{i+1}^* \tag{1 (a)}$$

$$mP_i^* \overset{K_a}{\rightleftharpoons} (P_i^*)_m \tag{1 (b)}$$

$$(P_i^*)_m + \quad M \xrightarrow{\quad x \quad} \text{no reaction} \tag{1 (c)}$$

where P_i^* denotes the non-aggregated unimeric active species, $(P_i^*)_m$ – the aggregated species, m – the aggregation degree, M – the monomer molecule, k_p – the rate constant of propagation, and K_a – the equilibrium constant of aggregation.

In the case when aggregated species dominate, e.g. when $m[(P_i^*)_m] \approx [I]_0$

$$K_a = \frac{[(P_i^*)_m]}{[P_i^*]^m} = \frac{[I]_0}{m[P_i^*]^m} \tag{2 (a)}$$

and

$$[P_i^*] = ([I]_0/mK_a)^{1/m} \tag{2 (b)}$$

Thus, the rate of monomer consumption is given by:

$$-\frac{d[M]}{[M]dt} = k_p(mK_a)^{-1/m}[I]_0^{1/m} \tag{2 (c)}$$

or, after integration and in the bilogarithmic coordinates, we have eventually:

$$t^{-1} \cdot \ln(\ln\frac{[M]_0}{[M]}) = \ln A - \frac{1}{m}\ln[I]_0 \tag{2 (d)}$$

where: $A = k_p(mK_a)^{-1/m}$, $[M]_0$ and $[M]$ denote the starting and instantaneous concentrations of monomer, $[I]_0$ – the starting concentration of initiator, and t – the polymerization time

Plotting the left hand side of eq. 2 (d) as a function of $\ln[I]_0$ the slope gives the degree of aggregation. However, this approach does not allow determination of K_a and k_p, but merely their product.

We found a way of determining both k_p and K_a, particularly when in the way described above the degree of aggregation (m) is known. This equation reads[6)]:

$$r_p^{1-m} = -m(K_a k_p)^{1-m} + k_p[I]_0 r_p^{-m} \tag{3}$$

where: $r_p = t^{-1} \cdot \ln([M]_0/M])$

Thus, by plotting $r_p^{\ 1-m}$ as a function of $[I]_0 \cdot r^{-m}$ one can obtain both k_p and K_a.

The generality of this solution allowed determining k_p and K_a for a few systems, that earlier were accessible only from numerical calculations[25].

This analytical solution can be used for any reaction system in which aggregated and non-aggregated species coexists and is not confined exclusively to the propagation accompanied by aggregation.

$$A + B \longrightarrow C \qquad (4\,(a))$$

$$nA \rightleftharpoons A_n \qquad (4\,(b))$$

$$A_n + B \xrightarrow{x} \text{no reaction} \qquad (4\,(c))$$

It is surprising that a large number of kinetic instances have been solved and are classified whereas this relatively simple scheme did not have an analytical solution

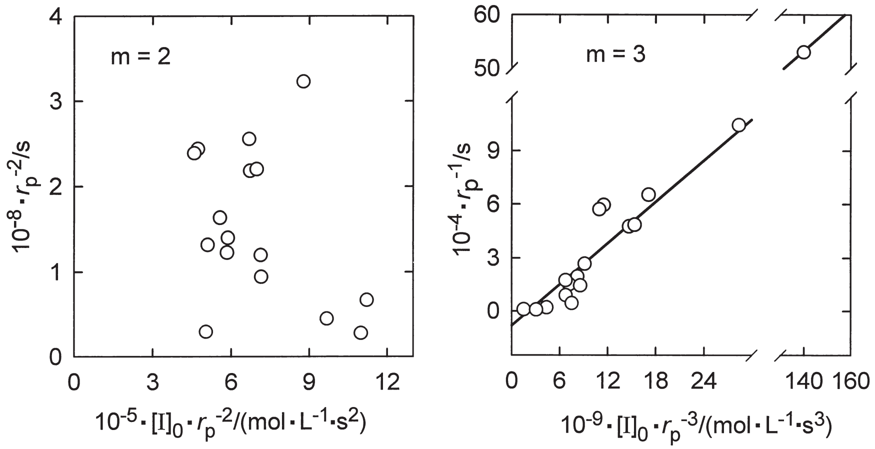


Fig. 4: Polymerization of εCL initiated with Et_2AlOEt (THF, 25°C). Test of eq. (3) for degree of aggregation m. Only for m=3 straight line was obtained as required. (Primary kinetic data taken from Ref. 7).

How powerful is this analytical approach is shown by comparison of two figures taken from our work (Fig. 4)[7]. Although we knew that the degree of aggregation is equal to 3 for polymerization conducted with diethyl aluminium alkoxide but we decided to test equation for the known correct value equal to 3 and to see whether it is conclusive by introducing an incorrect value equal to 2 for the aggregation number. First gives indeed the straight line as required whereas assuming an incorrect value does not give an expected straight line.

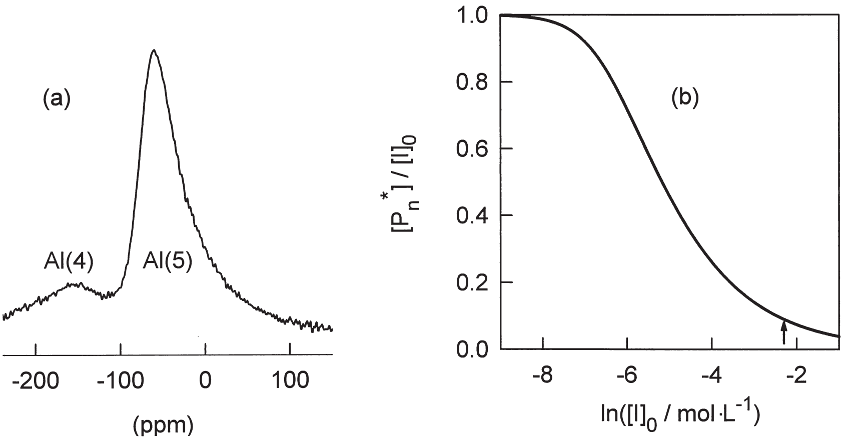
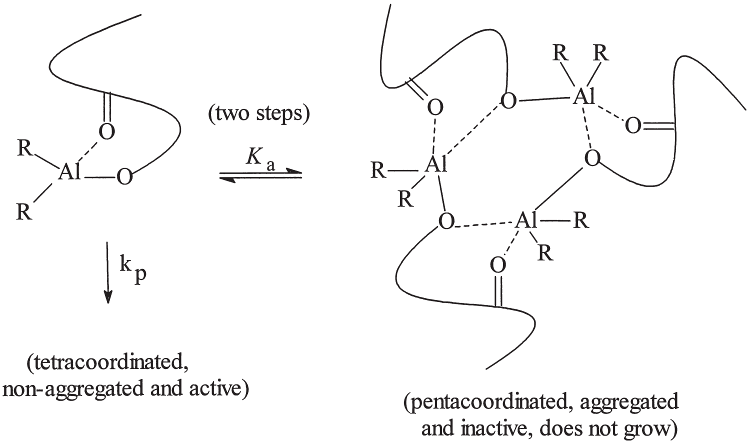


Fig. 5: (a) ^{27}Al NMR spectrum of polymerizing mixture: εCL/Et_2AlOEt/THF (+10 vol-% of C_6D_6). Al(4) and Al(5) indicate the absorption bands related to the tetra- and pentacoordinated Al-atoms, respectively (cf. Eq. (5)). Conditions: $[\epsilon CL]_0$ = 2 mol·L^{-1}, $[Et_2AlOEt]_0$ = 0.1 mol·L^{-1}, 25°C$^{26)}$. (b) Dependencies of the mole fraction of the unimeric, non-aggregated active centres ($[P_n^*]/[I]_0$) on their total concentration ($[I]_0$) as determined from the kinetic measurements for the εCL/Et_2AlOEt/THF system. Conditions: $[\epsilon CL]_0$ = 2 mol·L^{-1}, THF, 25°C. Arrow indicates $[P_n^*]/[I]_0$ obtained for $[I]_0$ = 0.1 mol·L^{-1} (Data taken from Ref. 7).

It was interesting to compare the determined proportion of the unimeric, actualy growing species with the proportion estimated from the ^{27}Al NMR spectrum. The corresponding spectrum is shown in Fig. 5 (a)$^{26)}$. There are two peaks, for tetra- and pentacoordinated aluminium. The estimated from the spectrum concentration of the tetracoordinated species is equal to ≈10% of the total, thus comparable with that determined from kinetics. The interconverting species can be shown as follows.



(5)

Presumably, the carbonyl oxygen atom, participating in solvation, comes from the first monomer unit of the chain attached to the Al.-atom.

Selectivity in Cyclic Esters Polymerization

The major side reactions in the polymerization of εCL and lactides (LA) are chain transfer with chain rupture. As it is well known, chain transfer proceeds to the own or foreign macromolecule. Both of these processes have been studied.

The first is relatively easy to study quantitatively. This is because the products of the chain transfer are cyclic compounds and their concentration can be measured. Thus, we have propagation and formation of cyclic oligomer, and if propagation involving monomer is practically irreversible (i.e. if $k_d \approx 0$ as in the case of ϵCL) then the kinetic scheme reads:

$$\begin{aligned} P_n^{\star} + M(1) &\xrightarrow{k_p} P_{n+1}^{\star} \\ P_n^{\star} &\underset{k_{-tr1}(x)}{\overset{k_{tr1}(x)}{\rightleftharpoons}} P_{n-x}^{\star} + M(x) \end{aligned} \tag{6}$$

where P_n^* denotes the growing polyester chain with $DP_n = n$, M(x) the macrocycle with $DP_n = x$, and $k_{tr1}(x)$ the rate constant of the unimolecular transfer (back-biting).

After introducing the selectivity parameter $\beta = k_p / k_{tr1}(x)$ for a given x-macrocycle we have[27,28)]:

$$\beta = \frac{k_p}{k_{tr1}(x)} = \frac{\ln \dfrac{[M(1)]_0}{[M(1)]}}{[M(x)]_{eq} \ln \dfrac{[M(x)]_{eq}}{[M(x)]_{eq} - [M(x)]}} \tag{7}$$

The larger the value of β the more selective is the process with a given active species. Selective - it means - there is more propagation steps per one step of cyclization which is not a desired reaction.

In Fig. 6 polymerizations proceeding on ionic and on covalent species are compared. On the alcoholate anion, before the monomer is consumed, there is already a large proportion of cylics, whereas when an aluminium based covalent active species are used there are no detectable cyclics when full monomer conversion is reached. Naturally, at equilibrium the composition of both systems should be the same, but it takes a long time in the covalent process.

Using the described kinetic approach we determined these ratios of k_p/k_{tr} for a few initiating systems and this ratio differs by a factor as large as 10^2. There are two phenomena involved, namely reactivity and steric hindrance. The higher the reactivity for species of comparable steric hindrance around growing species, like Sm trialkoxide and Al trialkoxide[29)] the lower the selectivity as it is often the case in chemical reactions. If, on the other hand, the reactivity is the same but steric hindrance differs, then for higher sterically hindered species the selectivity is better. This is the case of alkoxy Al dialkyls. For diisobutyl aluminium the selectivity is better than for diethyl derivative because for bulky substitents propagation is not affected anyhow, whereas chain has more difficulties is achieving the conformation needed for the reaction to occur [28)].

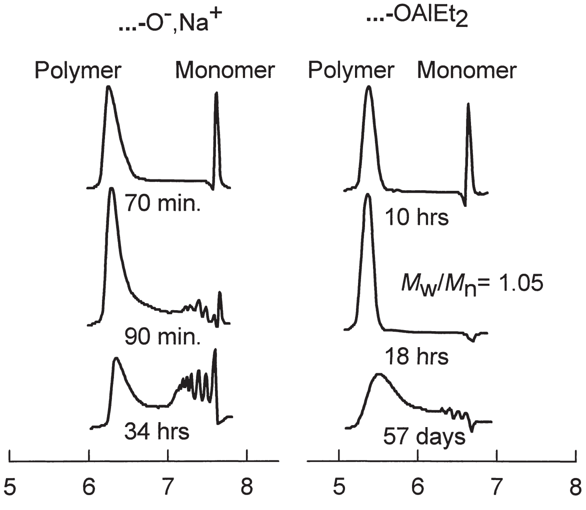
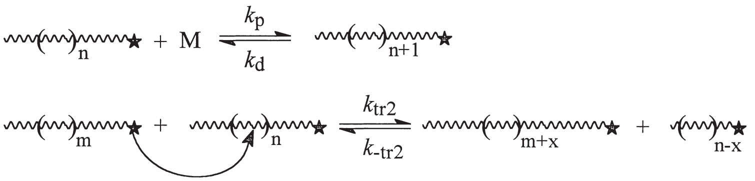


Fig. 6: GPC traces showing formation of macrocycles in polymerization of ε-caprolactone initiated with ionic and covalent species. $[\varepsilon CL]_0 = 0.5$ mol·L^{-1} , $[I]_0 = 5\cdot10^{-3}$ mol·L^{-1} , THF, 25°C. Polymerization times are indicated directly in the figure (Reproduced from Ref. 27).

The bimolecular transfer is a general problem of macromolecules with heteroatoms in the main chain (polyethers, acetals, esters, and amides). As far as esters are concerned, when one active macromolecule reacts with another one, then the two active ones are reproduced. In some other polymerizations, for instance reaction of two active ones may also produce one inactive and one with two active species. This is for instance the case of polyacetals.

Thus, in case of the polymerization of cyclic esters we have propagation and transfer with chain rupture of one kind; schematically:



(8)

where k_{tr2} denotes the rate constant of the bimolecular chain transfer.

Thus, the only change that is observed is broadening of molar mass distribution (MMD). Therefore k_{tr2} (or k_p/k_{tr2}) can be determined on the basis of the change of MMD as a function of monomer conversion. This problem was approached over 20 year ago by Russian authors when they studied polymerization of cyclic acetals[30)]. However, the monomodal distribution was assumed at that time, correct for the polymerization of cyclic acetals, where chain transfer is almost as fast or even faster than propagation. However, as it is shown in Fig. 7, for polymerization of lactide with tin^{II} butoxide, at certain monomer conversion the bimodality appears, and finally disappears when the monomer is consumed.

This is a general phenomenon, that was not considered earlier in polymer science. We are used to think, that in the polymerization process bimodality exclusively appears when there are two species, propagating with different rate constants and that do not exchange fast enough.

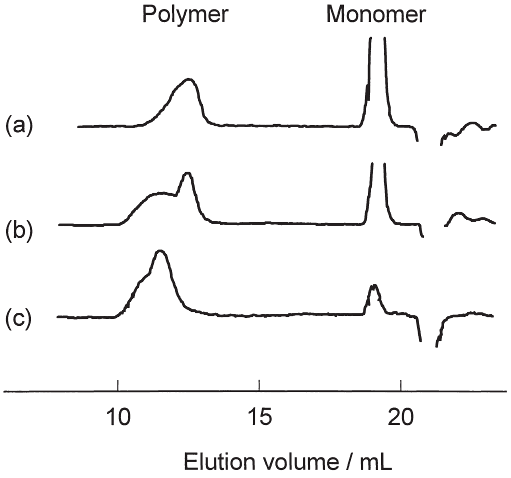


Fig. 7: Dependence of molar mass distribution on monomer conversion (α) in polymerization of L,L-dilactide initiated by $Sn(OBu)_2$. (a) $\alpha = 0.42$, $M_n = 3\cdot10^4$, $M_w/M_n = 1.18$ (b) $\alpha = 0.66$, $M_n = 4.7\cdot10^4$, $M_w/M_n = 1.40$. (c) $\alpha = 0.88$, $M_n = 6.3\cdot10^4$, $M_w/M_n = 1.53$. Polymerization conditions: $[LA]_0 = 3.0$ mol·L^{-1}, $[Sn(OBu)_2]_0 = 0.003$ mol·L^{-1}, THF at 80°C[26)].

In Fig. 8 the simulation of the MMD for conditions when k_p/k_{tr2} is high, i.e. for a relatively slow transfer is shown. Thus, chains are initiated at once and they grow, giving at the beginning close to Poisson distribution. They undergo transfer all of the time, but only approximately once for one hundred steps of propagation. A new population of macromolecules that participated in transfer adds slowly to the populations with Poisson distribution. The M_n of this population is the same, but M_w differs and this appears on the GPC traces. We used Monte Carlo simulation[11,13)], generating a number of nomograms (Fig. 9 (a)), giving finally the dependence of MMD on monomer conversion for the kinetic scheme 8. Thus, if for a given ratio of starting concentrations of monomer to initiator the dependence of M_w/M_n as a function of conversion is determined, the k_p/k_{tr2} can be found from the nomogram. This is shown in the Fig. 9 (b), for various covalent alkoxides. Lines were calculated for a given ratio of k_p/k_{tr2} and points are experimental. On this basis it was possible to determine k_p/k_{tr2} for a given system.

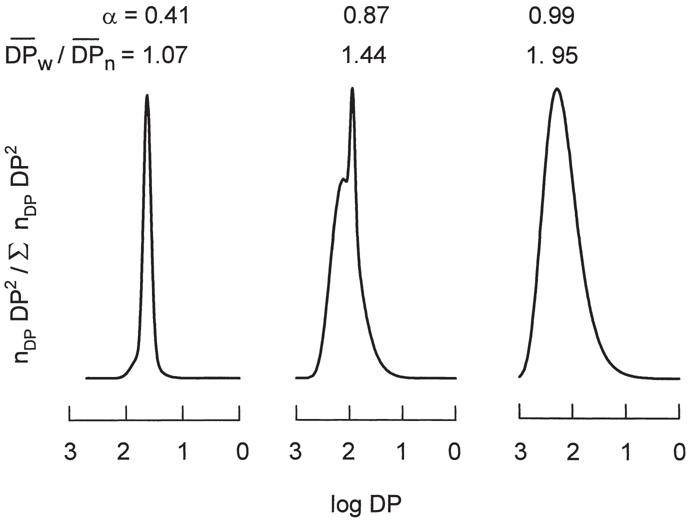


Fig. 8: Computed (Monte-Carlo method) chain length distributions (DP_w/DP_n) as a function of monomer conversion degree (α). Conditions: $[M]_0/[I]_0 = 10^2$, $k_p >> k_d$ (Reproduced from Ref. 11).

Divalent tin has particularly good selectivity. Although we are looking for ways of getting even better selectivity, from a practical view point it is not so much important for a homopolymer to have a narrow distribution. Slowing down chain transfer is, however, important for the well controlled block copolymers and other controlled architectures.

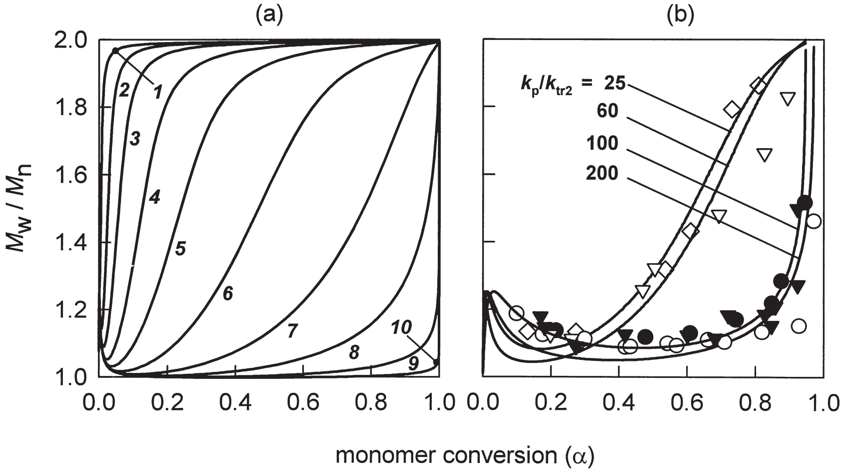


Fig. 9: (a) Computed dependencies of M_w/M_n on degree of monomer conversion (α). Conditions: $k_p/k_{tr2} = 10^{-2}$ (1), $2 \cdot 10^{-1}$ (2), $5 \cdot 10^{-1}$ (3), 2 (4), 10^1 (5), $5 \cdot 10^1$ (6), $2 \cdot 10^2$ (7), 10^3 (8), $5 \cdot 10^3$ (9), $2 \cdot 10^4$ (10) (b) Dependencies of M_w/M_n on α determined for L,L-lactide (LA) polymerization initiated with (in brackets are given $[M]_0/[[I]_0$ ratios in which $[I]_0$ denotes starting concentration of the alkoxide group): (◇) Bu_3SnOEt, (▽) $Fe(OEt)_3$, (▼) $Al(O^iPr)_3$, (●) $Sn(Oct)_2$, (○) $Sn(OBu)_2$, THF solvent, 80°C ($[LA]_{eq} = 5.5 \cdot 10^{-2}$ (as determined in Ref. 31). Points experimental, lines computed assuming k_p/k_{tr2} = 200, 100, 60, and 25, respectively[26)].

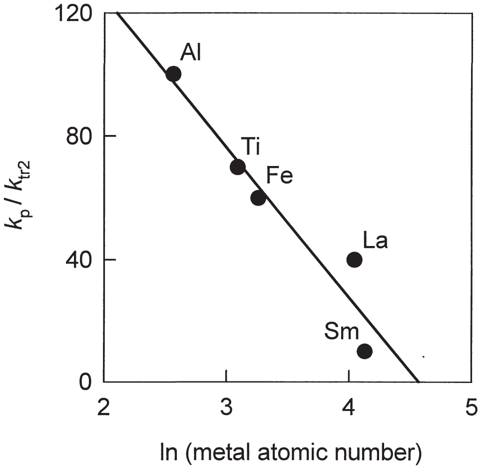


Fig. 10: Dependencies of k_p/k_{tr2} on the atomic number of the metal atoms involved in active species, determined in polymerizations of L,L-dilactide initiated with covalent metal alkoxides (THF, 80°C). (Data taken from Ref. 10).

Now we can further correlate the determined rate constants as a function of the bond stregth in alcoholates - this is related to the metal atomic number (Fig. 10). This dependence is observed for several alkoxides, but the alkylalkoxides do not fall on the same line[10)] .

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References

(1) S. Slomkowski, S. Penczek, *Macromolecules* **13**, 229 (1980)
(2) A. Deffieux, S. Boileau, *Macromolecules* **9**, 369 (1976)
(3) S. Slomkowski, S. Penczek, *Macromolecules* **9**, 367 (1976)
(4) A. Duda, S. Penczek, *Macromol.Rapid Commun.* **67**, 196 (1995)
(5) A. Duda, S. Penczek, *Macromolecules* **28**, 5981 (1995)
(6) S. Penczek, A. Duda, *Makromol.Chem., Macromol.Symp.* **47**, 127 (1991)
(7) A. Duda, S. Penczek, *Macromol.Rapid Commun.* **15**, 559 (1994)
(8) T. Biela, A. Duda, *J.Polym.Sci., Part A: Polym.Chem.* **34**, 1807 (1996)
(9) A. Kowalski, A.Duda, S. Penczek, *Macromolecules* **31**, 2114 (1998)
(10) J. Baran, A. Duda, A. Kowalski, R. Szymanski, S. Penczek, *Macromol.Symp.* **128**, 241 (1998)
(11) J. Baran, A. Duda, A. Kowalski, R. Szymanski, S. Penczek, *Macromol.Rapid Commun.* **18**, 325 (1997)
(12) S. Penczek, A. Duda, R. Szymanski, *Macromol.Symp.* **132**, 441 (1998)
(13) R.Szymanski, *Macromol.Theory Simul.* **7**, 27 (1998)
(14) (a) S. Slomkowski, *Polymer* **27**, 71 (1986); (b) unpublished data
(15) A. Duda, *J.Polym.Sci., Part A: Polym.Chem.* **30**, 21 (1992)
(16) S. Boileau, *Am.Chem.Soc., Symp.Ser.* **166**, 283 (1981)
(17) J. Haggiage, P. Hemery, S. Boileau, R. W. Lenz, *Polymer* **24**, 576 (1983)
(18) S. Sosnowski, S. Slomkowski, S. Penczek, *Makromol.Chem.* **192**, 735 (1991)
(19) S. Sosnowski, S. Slomkowski, S. Penczek, *J.Macromol.Sci., Chem.* **A20**, 979 (1983)
(20) S. Slomkowski, S. Penczek, *Am.Chem.Soc., Symp.Ser.* **166**, 271 (1981)
(21) R. N. Young, L. J. Fetters, J. S. Huang, R. Krishnamoonti, *Polym.Intnl.* **33**, 217 (1994)
(22) S. Bywater, *Polym.Intl.* **38**, 325(1995)
(23) M. Szwarc, *J.Polym.Sci., Part A: Polym.Chem.* **37**, 873 (1998)
(24) S. Sosnowski, S. Slomkowski, S. Penczek, L. Reibel *Makromol.Chem.* **184**, 2159 (1983)
(25) A. Duda, S. Penczek, *Macromolecules* **27**, 4867 (1994)
(26) A. Duda, S. Penczek, in preparation
(27) A. Hofman, S. Slomkowski, S. Penczek, *Makromol.Chem., Rapid Commun.* **8**, 387 (1987)
(28) S. Penczek, A. Duda, S. Slomkowski, *Makromol.Chem., Macromol.Symp.* **54/55**, 31 (1992)
(29) S. Penczek, A. Duda, *Macromol.Symp.* **107**, 1 (1996)
(30) B.A. Rozenberg, V.I. Irzhak, N.S. Enikolopyan, *"Interchain Exchange in Polymers"* (in Russian), Khimya, Moscow 1975
(31) A. Duda, S. Penczek, *Macromolecules* **23**, 1636 (1990)