

POLIMERY

CZASOPISMO POŚWIĘCONE CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

Professor **Andrzej Duda** In Memoriam

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DOI: dx.doi.org/10.14314/polimery.2017.239

Abstract: This paper is describing major scientific achievements of the recently late Professor Andrzej Duda, Chairman of the Department of Polymer Chemistry of The Centre of Molecular and Macromolecular Studies of Polish Academy of Sciences. Professor Duda published over 100 scientific papers and has given several dozens of plenary and invited lectures at the scientific symposia. However, in the present paper, we are mostly describing accomplishment that all of us, and also Professor, have considered as his seminal work, that solved a long time controversial subject. Namely, how to influence reactivities of chiral monomers, using chiral catalysts. Professor Duda had shown, and this subject is mostly described, that reactivity of a chiral monomer can be unchanged (when compared with an achiral catalyst) when polymerized with catalyst of the same chirality and may be many times depressed (the feature highly valuable in several instances) when polymerized with a catalyst with an opposite chirality. This feature is very important in the copolymerization processes, when chiral monomer is much more reactive than the other comonomer. Besides, some other contributions of Professor Duda to Polymer Sciences are also, although briefly mentioned. Full list of papers is given in the second part of the paper.

Keywords: chiral monomers, comonomers, reactivity, polymerization, rate of copolymerization.

Pamięci Profesora **Andrzeja Dudy**

Streszczenie: Przedstawiono najważniejsze osiągnięcia naukowe Profesora Andrzeja Dudy, wieloletniego Kierownika Zakładu Chemii Polimerów Centrum Badań Molekularnych i Makromolekularnych Polskiej Akademii Nauk. Profesor Duda opublikował ponad 100 prac naukowych, wygłosił kilkadziesiąt wykładów na zaproszenie, w tym także wykłady plenarne na prestiżowych konferencjach międzynarodowych. W niniejszym, krótkim omówieniu prac Profesora skupiliśmy się przede wszystkim na dwóch zagadnieniach, spośród których szczególnie pierwsze było według naszego przekonania głównym osiągnięciem, rozwiązującym ważny problem dotyczący kopolimeryzacji monomerów chiralnych. Profesor Duda, po raz pierwszy w chemii polimerów, ustalił że polimeryzacja chiralnych monomerów przebiega niezmiennie wobec katalizatorów achiralnych oraz chiralnych o takim samym znaku jak znak monomeru, natomiast zastosowanie katalizatora o odwrotnej chiralności pozwala na znaczne zmniejszenie szybkości polimeryzacji. Jest to zjawisko o zasadniczym znaczeniu w kopolimeryzacji, szczególnie kiedy chiralny monomer jest znacznie bardziej reaktywny niż drugi komonomer. Mniej szczegółowo omówiono inne osiągnięcia Profesora Andrzeja Dudy, dodano też pełną bibliografię Jego prac.

Słowa kluczowe: monomery chiralne, komonomery, reaktywność, polimeryzacja, szybkość kopolimeryzacji.

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This short paper is devoted to the memory of the late Professor Andrzej Duda. A long time our principal, co-worker and friend, with whom we shared several common interests and fascinations of the scientific works and music.

The paper is composed of two parts. In the first one the major personal scientific achievements of Andrzej are described and in the second one the complete bibliography is compiled.

Whenever, after long time, we are looking back on these hundreds of papers we have published, we can easily find out just a few ones (if we are lucky) that have made impact on the field of our activity. With this idea in mind we are describing in some details just a few contributions of Andrzej.

In the last decades Andrzej was involved in numerous endeavors related to polylactides (PLA). Both scientific and organizational of one of the largest project in polymer research in Poland, BIOPOL (43 million PLN) that eventually has been finalized with construction of two pilot plants, namely at the Institute of Biopolymers and Artificial Fibers in Lodz and in the Chemistry Department of the Warsaw Technical University. Andrzej was also involved in the next step – transfer of these technologies to the large industrial scale. None would be possible without his knowledge and leadership. However the major passion of Andrzej was research, mostly understanding the polymerization processes on the molecular level and an attempt to describe the studied reactions in the quantitative way. He, actually, came to the Centre of the Academy from the school of kinetics at the Institute of Radiation Research of the Lodz Technical University headed at that time by Professor Jerzy Kroh. This high level education enlarged the research possibilities of the Department of Polymer Chemistry of the Centre that Andrzej joined in 1976.

The most significant, personal scientific achievements of Andrzej have been realized during the last two decades. He believed, that the expression “polylactide is the polymer of the XXIst century” is not merely playing with words. He believed that finally, this polymer, biobased, biocompatible and biodegradable will be one of the largest on the industrial scale in the near future and that it will also be needed in Poland with its developed agriculture. The total world production of PLA is already close to 0.5 million tons/year.

Thus, Andrzej was looking in improving the existing process of polylactide synthesis, in the way of understanding the elementary reactions, and also on the enlarging the scope of the PLA applications, as well, as mentioned above, in finding ways for PLA to the Polish Industry.

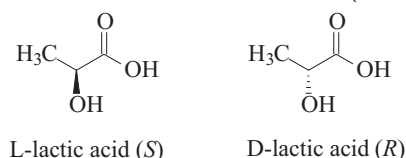
The major, personal contribution to the polymer chemistry of Andrzej follows from his seminal work on the influence of chirality of the catalytic ligands on the homo- and copolymerization of lactides.

In order to clearly comprehend the importance of these works a short further introduction is needed.

STEREOCONTROLLED POLYMERIZATION OF RACEMIC LACTIDE (LA) WITH CHIRAL INITIATORS

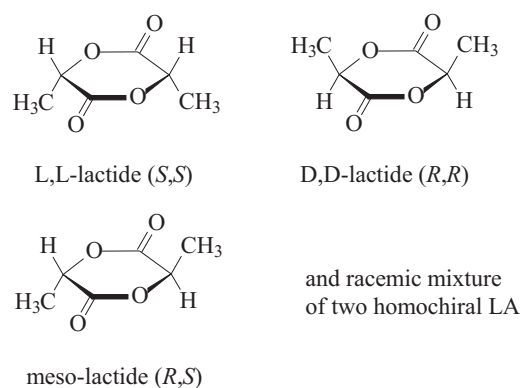
This is an abbreviated title of one of the papers by Andrzej that opened a novel field of research of LA polymerization [1].

As it is known, lactide (LA) is a cyclic dimer of lactic acid, which has one chiral carbon atom (Scheme A).



Scheme A. L-lactic acid and D-lactic acid

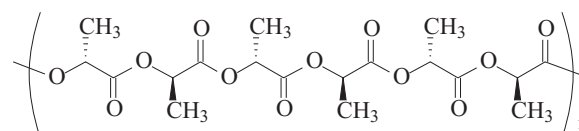
Thus, there are three isomers of LA and racemic mixture, as shown in Scheme B, the two homochiral ones with two identical chiral centers each, meso-lactide, with two different chiral centers, and racemic mixture of two homochiral LA.



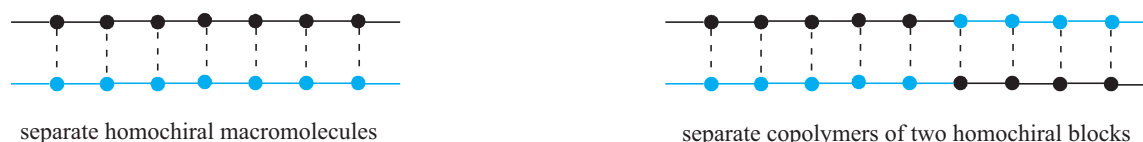
Scheme B. Stereo structures of lactides

In this paper only (*S,S*)-lactide and (*R,R*)-lactide names will be applied as it is easier to follow the stereocontrolled polymerizations with catalysts fitted with chiral ligands, although, in the current polymer literature mostly names L,L-lactide (or L-lactide) and D,D-lactide are respectively used.

The major industrial polymer is based on (*S,S*)-lactide, (*S,S*)-LA, that is produced by fermentation (in a similar way as ethyl alcohol) from carbohydrates. This could be sugar, but at the principal producer (Cargill Co.) the waste products of the corn production are the raw materials. There is also a synthetic way, which leads to the racemic mixture of two homochiral lactides. The polymer of (*S,S*)-LA {poly[(*S,S*)-LA]} is industrially prepared in the highly stereospecific way, *i.e.*, with (almost) complete retention of configuration of (*S,S*)-LA. This is, most obviously leading to practically pure isotactic polymer, *i*-poly[(*S,S*)-LA] (later in the text prefix *i* is omitted) (Scheme C).



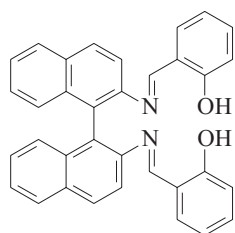
Scheme C. Structure of poly[(*S,S*)-LA], formed from (*S,S*)-LA with retention of configuration



Scheme D. The pictograms of separate homochiral macromolecules and separate copolymers of two homochiral blocks, both forming stereocomplexes

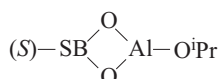
Poly[(*S,S*)-LA] is partially crystalline and melts $\sim 180^\circ\text{C}$. To increase its toughness a few percent of (*R,R*)-LA are added. Its physical properties bear resemblance of polystyrene. The melting temperature is nevertheless not high enough for several applications. However, it is known, that stereocomplex composed of two homochiral poly(LA), one poly[(*S,S*)-LA] and one poly[(*R,R*)-LA], in which van der Waals interactions give sufficiently strong bonding, has melting temperature much higher, around 210°C . Having melting temperature in this region is important for several applications (e.g. fibers). Andrzej has asked a question: let us suppose that we have a racemic mixture – how to get the stereocomplex in “one pot” synthesis. Solution of this, at that time basic question, has been given in his work published in JACS [1]. As it is stated in this paper, the stereocontrolled polymerization of lactides had already been known, but not the synthesis of stereocomplexes the way discovered by Andrzej [1]. The novelty of the Andrzej approach had been based on an idea of preparation of the block copolymer of poly[(*S,S*)-LA] and poly[(*R,R*)-LA], assuming that such diblock copolymer would have even better properties when converted into stereocomplex, that merely a stereocomplex from a mixture of poly[(*S,S*)-LA] and poly[(*R,R*)-LA]. The pictograms of these two different solutions are given in Scheme D.

Thus, in order to realize practically this idea Andrzej applied catalysts with two different chiral ligands, one with (*S*)- and one with (*R*)-configuration to the consecutive polymerization of racemic mixture of lactides (*S,S*) and (*R,R*). The structure of the ligand in the prochiral form is shown in Scheme E.



Scheme E. Structure of prochiral 2,2'-[1,1'-binaphthyl-2,2'-diyl-bis-(nitrylomethylidene)]diphenol – Schiff base [SB(OH)₂]; related chiral ligands have been applied for the synthesis of chiral catalysts in reaction with Al(OⁱPr)₃, used then in the synthesis of poly[(*S,S*)-LA]-*b*-poly[(*R,R*)-LA] copolymer; depending on the position of naphthyl rings there are (*S*)- or (*R*)-stereoisomers, respectively

The two-steps-one-pot polymerization of *rac*-LA was initiated first by addition of



(*S*)-2,2'-[1,1'-binaphthyl-2,2'-diyl-bis(nitrylomethylidene)]diphenol [(*S*)-SB(OH)₂] to Al(OⁱPr)₃. Ligand reacted with Al(OⁱPr)₃, giving chiral catalyst/initiator. This one polymerized in stereoselective way the (*S,S*)-LA and when its polymerization was almost complete (measurements by polarimetry) then equimolar quantity of (*R*)-SB(OH)₂ was introduced, replacing, at least partially, the (*S*)-SB ligand by (*R*)-SB ligand, and starting polymerization of the second, (*R,R*)-LA, stereoisomer.

Thus, first poly[(*S,S*)-LA] is formed, and then, to the same macromolecule the second block of poly[(*R,R*)-LA] is attached. In this way a block copolymer poly[(*S,S*)-LA]-*b*-poly[(*R,R*)-LA] results. It forms mostly with its neighbors the corresponding stereocomplexes. In Fig. 1, borrowed in part from paper in [1] and slightly modified, the kinetic course of the block copolymerization is illustrated.

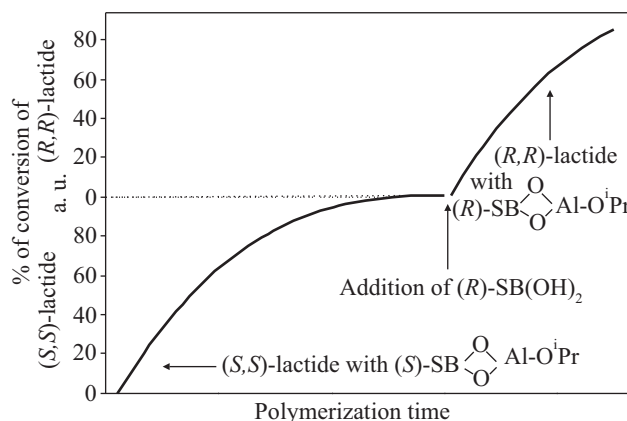
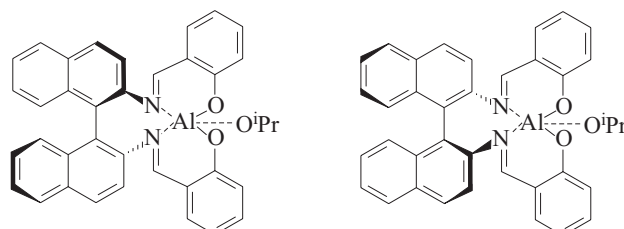


Fig. 1. Simplified kinetics of block copolymer and stereocomplex formation; stereoselective polymerization of racemic LA: first (*S,S*)-LA and then (*R,R*)-LA in consecutive order, governed by $>\text{AlOR}$ catalyst, first with (*S*)-ligand and then with (*R*)-ligand; the detailed data (polymerization conditions) are given in the original paper [1]

To complete this part of report, structures of the catalysts with chiral ligands, after reaction with Al(OⁱPr)₃, are given in Scheme F.



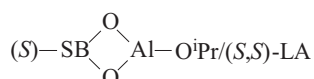
Scheme F. Structures of catalysts – $>\text{AlO}^i\text{Pr}$ with chiral ligands: (*R*)-SBO₂-AlOⁱPr (left) and (*S*)-SBO₂-AlOⁱPr (right)



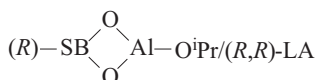
Scheme G. The structure of stereocomplex formed by block/gradient macromolecules containing long enough consecutive units of (S,S)-LA and of (R,R)-LA for stable interactions, required for stereocomplex formation

The melting temperature T_m of the resulting stereoblock copolymer of two block copolymers is close to 240 °C, thus higher than the known values of T_m for stereocomplexes prepared earlier, by mixing two homochiral homopolymers of PLA.

In the further, more detailed studies, which have not changed the basic idea and importance of the described above work, kinetics of polymerization carried out with



have shown 28 : 1 preference for the polymerization of (S,S)-LA over (R,R)-LA. Similar results have been observed for the



pair: preference over (S,S)-LA. Thus, the purity of the block copolymer was influenced by gradient copolymers formation. The imperfect stereocomplex, in which block copolymers have inclusions of foreign units, namely S units in polyR block and R units in polyS block (respectively, blue points in red chain and red points in blue chain), is shown in Scheme G (taken from the unpublished work of Andrzej).

COPOLYMERIZATION OF LA WITH ϵ -CAPROLACTONE (CL)

After understanding of the influence of stereocontrol on polymerization of chiral lactides, Andrzej had moved to another unsolved at that time problem and crucial for the progress in polymerization of LA. It is related to the copolymerization of LA with ϵ -caprolactone (CL). Poly- ϵ -caprolactone (PCL) is another important industrial biodegradable polymer for biomedical and pharmaceutical applications. Poly(S,S)-LA (PLA) and PCL differ substantially in their physical properties, PLA is a stiff plastic, and PCL may be elastic. Besides, they differ also in the rates of biodegradation. For example, PLA has a much shorter half-time *in vivo* (a few weeks) than PCL (one year). This comparison of the rates of biodegradation is for a certain shape of the samples and other conditions that are comparable. Besides, PCL is permeable to many drugs with low molecular mass, whereas PLA is not. Thus, the LA/CL copolymerization enables the properties of the resulting polyester to be tuned by varying the composition and the mode of distribution of the comonomer units. However, the ratios of the rates of the monomers consumption during copolymerization at the usual copolymerization conditions differ to such an extent, that, if transesterification is avoided, rather block

copolymer is prepared then copolymer of statistical distribution of the comonomer units. This phenomenon had been known starting from the works of Teyssié [2] and Bero [3] and is illustrated in Fig. 2.

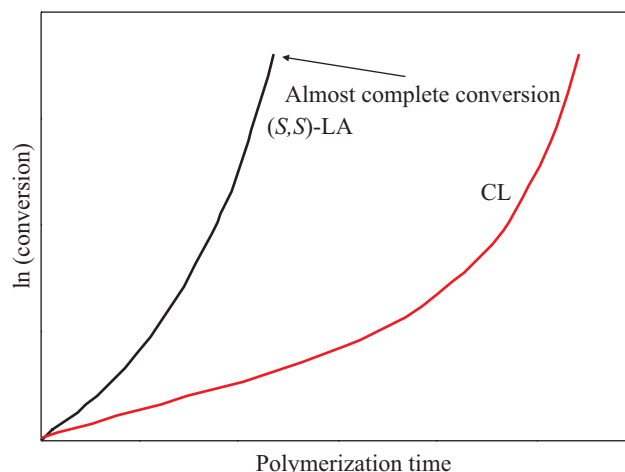
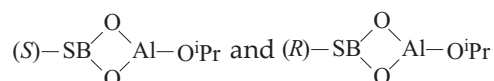


Fig. 2. Rates of consumption of (S,S)-LA and CL in a typical copolymerization catalyzed with $\text{Al}(\text{O}^i\text{Pr})_3$ (modified from [4])

(S,S)-LA is polymerizing first and appreciable consumption of CL starts when polymerization of (S,S)-LA is almost over. There was no satisfactory explanation for this behavior [in this review an attempt to explain prevailing reactivity of (S,S)-LA in copolymerization will be given]. This result was surprising, since in homopolymerizations this is CL that is polymerizing many times faster than (S,S)-LA [at least, with $\text{Al}(\text{O}^i\text{Pr})_3$ – the catalysts studied mostly at that time]. At the early and pioneering works, like in papers by Teyssié [2], it has been first assumed that a difference in basicities governs the ability of CL and (S,S)-LA to react with active species in copolymerization. However, the measured basicities of CL and (S,S)-LA (measured with proton attraction) were found to be too small to be an explanation. In order to get the statistical copolymer it was, thus, necessary-to decrease in copolymerization the rate of (S,S)-LA consumption as compared with CL consumption. Andrzej has done it in an ingenious way by playing with chirality of ligands attached to the Al catalyst [4]. Results are shown in two figures, Fig. 3 and Fig. 4. The first one gives comparisons of the rates of homopolymerization of CL (achiral), that is identical with $>\text{AlO}^i\text{Pr}$ initiator with (S)- and (R)-ligands



with rates of homopolymerization of (S,S)-LA with the same catalyst and also with (S)-ligand and (R)-ligand. Polymerization of (S,S)-LA has been found much slower

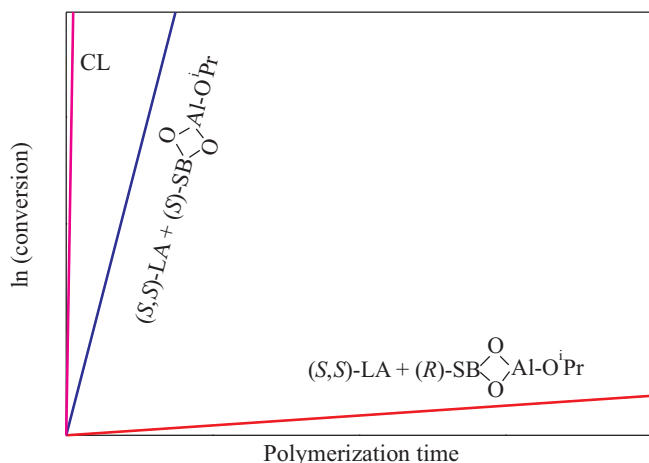


Fig. 3. The rates of homopolymerizations of (S,S)-LA and CL catalyzed by $\text{Al}(\text{O}^i\text{Pr})_3$ with chiral ligands; CL with either (S)- or (R)-ligand gives identical rates; (S,S)-LA with (R)-ligand (opposite chirality-heterochiral) polymerizes much slower than with (S)-ligand (the same chirality-homochiral); conditions of polymerization are given in the original paper [4]

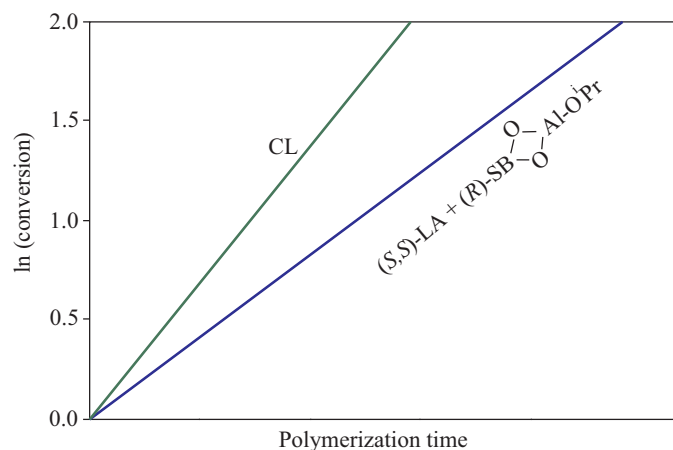


Fig. 4. The rates of (S,S)-LA and CL consumptions during copolymerization when catalyst is with (R)-ligand; now, (S,S)-LA consumption is slowed down sufficiently and becomes comparable to the rate of CL consumption; conditions as in Fig. 3 [cf. Fig. 1, where with achiral catalyst the relative rates are in the opposite order: (S,S)-LA is then much faster] (modified from [4])

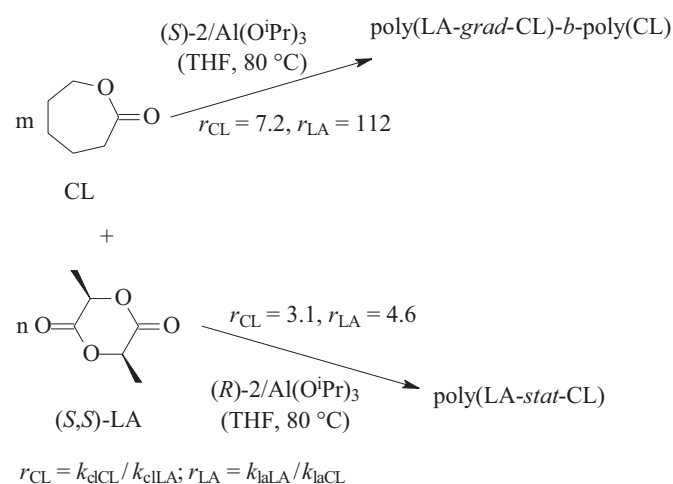
with (R)-ligand than with (S)-ligand. The use of two different ligands [“homo” and “hetero”, since this is (S,S)-LA] was based on results described in the previously cited work of Andrzej [1]. As it is seen from this schematic presentation in Figs. 3 and 4 (although copying exactly the actual data), Andrzej has found, for the first time, a way to keep with the same catalyst the rate of CL unchanged and the rate of polymerization of (S,S)-LA very much decreased, when catalyst with the heteroligand [(R) for the (S,S)-LA] was used. In this way a route was established to attain comparable rates of consumption of both comonomers in copolymerization.

Having established such a large difference in the rates of homopolymerization when (S,S)-LA is polymerized in the presence of catalyst with (S)-configuration or with (R)-configuration, the next, logically natural step, was

comparison of the rates of both monomers consumption at the copolymerization conditions when (R)-ligand (giving a low rate of LA homopolymerization) is used. This comparison of copolymerization of CL with (S,S)-LA [catalyst with (R)-ligand] is shown in Fig. 4.

Thus, comparison of Fig. 3 and Fig. 4 clearly shows the result of this important reverse of rates, having its roots in the earlier work of Andrzej [1], when, for the first time it has been observed, that for a chiral monomer the rate of polymerization depends dramatically on the chirality of catalyst (the applied ligand). Polymerization is fast, when the catalytic unit and monomer have identical chirality, whereas when chiralities are different, then the rate is much lower. Although further, more quantitative work would be needed along these lines, the general observation is a corner stone of understanding in which way the rates of polymerization of chiral monomers could be altered. It may well be a general rule, although there is no quantitative data from the other systems yet.

The results shown in pictures above are illustrated in Scheme H, borrowed from the Andrzej paper [4].

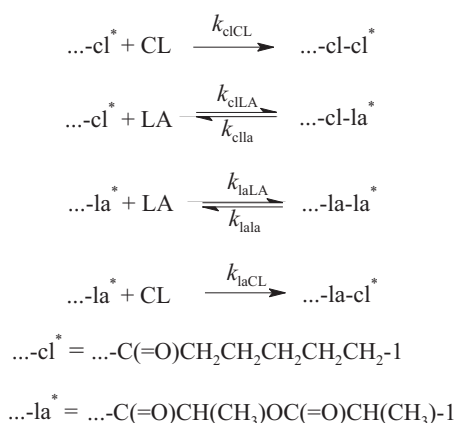


Scheme H. The influence of the alteration of active centers configuration on the reactivity ratios, *vic*, copolymers composition

Both systems studied in THF solvent, at 80 °C. The corresponding elementary reactions pertinent to Scheme H are given in Scheme I.

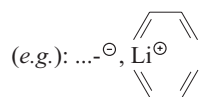
The values of the reactivity ratios given above, like r_{CL} and r_{LA} are rather apparent, since are calculated for the scheme without taking into account the reversibility of the propagation and possible aggregations. Schemes H and I are illustrating the reactions taking place, and could formally describe the course of copolymerization, but not yet explaining the reasons for the quantitative ratios of rates of these reactions.

During discussions in our group, at the early 2000, of the possible reason of the domination in copolymerization of (S,S)-LA [with (S)-SBO₂-Al(OⁱPr)], which is much slower in homopolymerization than CL, we turned to the well-known anionic copolymerization of styrene with 1,3-butadiene in non-polar solvents and with Li⁺ coun-



Scheme I. Elementary reactions related to Scheme H

terion. In this system, recently reexamined by van Beylen [5], butadiene is reacting first and only when it practically reacted, styrene starts to polymerize, although in homopolymerizations this is styrene that is much faster. The original explanation came from Korotkov [6], who assumed, that butadiene (B), because of its structure, may preferentially solvate the ion pairs, not allowing styrene (S) to approach the active species (Scheme K).

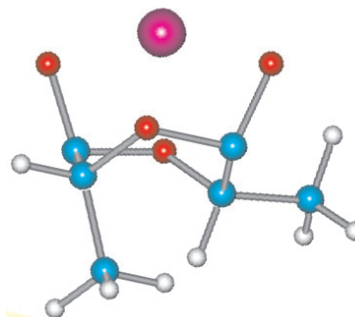


Scheme K. Solvation of active species by butadiene molecules related to the proposal of Korotkov [6]

This attractive explanation has been challenged and analyses of homo- and crosspropagations, measured independently [7], have shown, that $\sim s^{\ominus}, \text{Li}^{\oplus}$, is fast converted into $\sim sb^{\ominus}, \text{Li}^{\oplus}$, with a very large rate constant k_{sb} , which, in turn, is larger than k_{bs} . Although k_{ss} is greater than k_{bb} , but practically all of the active species are ended up with butadiene molecule. Thus, this is the largest rate of crosspropagation (butadiene to $\sim s^{\ominus}, \text{Li}^{\oplus}$ active species) that is mostly responsible for the observed phenomenon. However, as pointed out by van Beylen, even this explanation is not sufficient, since active species may form various aggregates, and the formal (apparent) rate constants are in fact products of the real rate constants and the aggregation constants, as discussed also in detail by Elias [8].

These data of the styrene/butadiene copolymerization are given in order to show, how difficult it is to properly describe such a relatively simple system and to understand better what could happen for the copolymerization of CL with (S,S)-LA, when not altered by influence of ligands.

Similar approach to explain usual copolymerization of (S,S)-LA with CL [not altered by (R)-ligand] is tempting and has been first taken into consideration. Unfortunately, the rates of crosspropagations have not been measured for the (S,S)-LA-CL pair and it is not easy to accept similar scheme as described above for styrene/butadiene, since it would require, that the fastest reaction is addition



Scheme L. Conformation of (S,S)-LA with two ester groups directed towards active species, as proposed (unpublished) at the lecture given in 2005 (to be published in the review paper, in preparation)

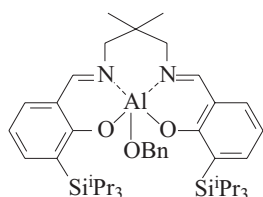
of (S,S)-LA to the active species $\dots\text{-cl}^*$ and also to the active species $\dots\text{-la}^*$. During these discussions with Andrzej (unpublished), it was thus further assumed, that perhaps, rather like in the proposal of Korotkov, it is (S,S)-LA that is blocking active sites of both kinds. (S,S)-LA has been known indeed to exist in various boat conformations [9, 10] that could engage, as we theorized, both ester groups in interaction with active centers. Therefore, simple measurements of basicities of (S,S)-LA and CL, discussed above and engaging only one ester group could be irrelevant.

Thus, perhaps (S,S)-LA could be converted in the vicinity of the active centers to the most energetically favorable conformation, that may differ from the privileged boat conformations when no interaction is involved [9, 10]. At that time we proposed structure, shown in Scheme L, with two ester groups directed toward the active species, much larger than hydrogen atom, (unpublished, presented at the 8th Hellenic Polymer Conference, Crete, 2005).

Thus, in homopolymerization CL is faster, mostly due to the absence of steric hindrance and in copolymerization it is (S,S)-LA that prevails, perhaps solvating specifically active species and not allowing CL to react by restricting its approaching to the active species. However, studies of the same (formally) system: styrene-1,3-butadiene is much more advanced and bring more sophisticated treatment of similar copolymerization system, in which monomer faster in homopolymerization is becoming slower in copolymerization.

Whatever is the proper explanation of the differences in the rates of reactions in homo- and copolymerization of (S,S)-LA with CL, Andrzej has shown, for the first time, how to prepare various kinds of copolymers from (S,S)-LA and CL, by altering the rate of polymerization of (S,S)-LA in its copolymerization with CL.

Since the paper of Andrzej appeared, it was followed by related approaches, attempting to decrease the reactivity of (S,S)-LA in copolymerization with CL. Thus, the approach of (S,S)-LA to the (e.g.) Al center should be decreased to the larger extent than the rate of CL addition. Thus, Nomura [11], a few years after the paper of Andrzej was published, has used achiral ligand, otherwise of the structure used by Andrzej, but more sterically hindered, in order to hamper the addition of more sterically demanding (S,S)-LA.



Scheme M. Structure of the sterically hindered ligand used by Nomura for controlled, statistical copolymerization of (*S,S*)-LA with CL

This highly sterically hindered ligand (structure shown in Scheme M) decreased the rate of LA approach to such an extent, that statistical copolymerization of LA with CL became possible. Nomura gave a nice picture, which is shown below, explaining why the LA approach to $>AlOR$ is hindered (Scheme N).

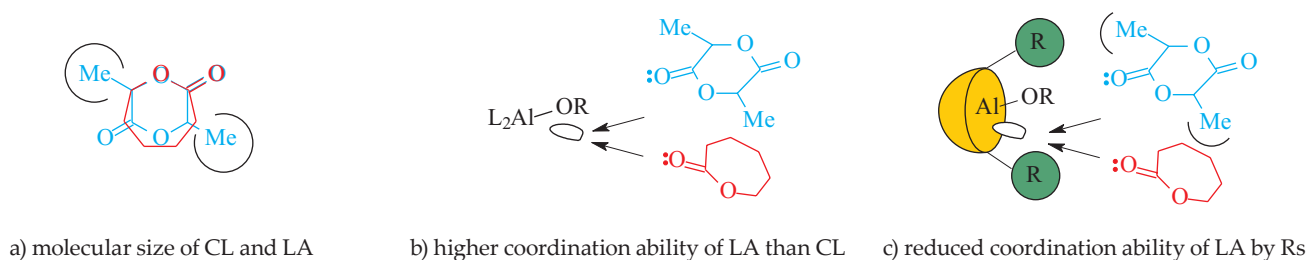
However, when we are looking on this picture by Nomura then it is not clear, why in (b) LA has higher ability for coordination, when only one ester group is involved. We rather think, that it is more proper to take into consideration the boat conformation of (*S,S*)-LA, as we are proposing in Scheme L. Then, if (*S,S*)-LA is presented as in Scheme L, the picture (c) from Nomura is easier to comprehend.

The described above pioneering works of Andrzej, based on the discovery of the influence of catalysts chi-

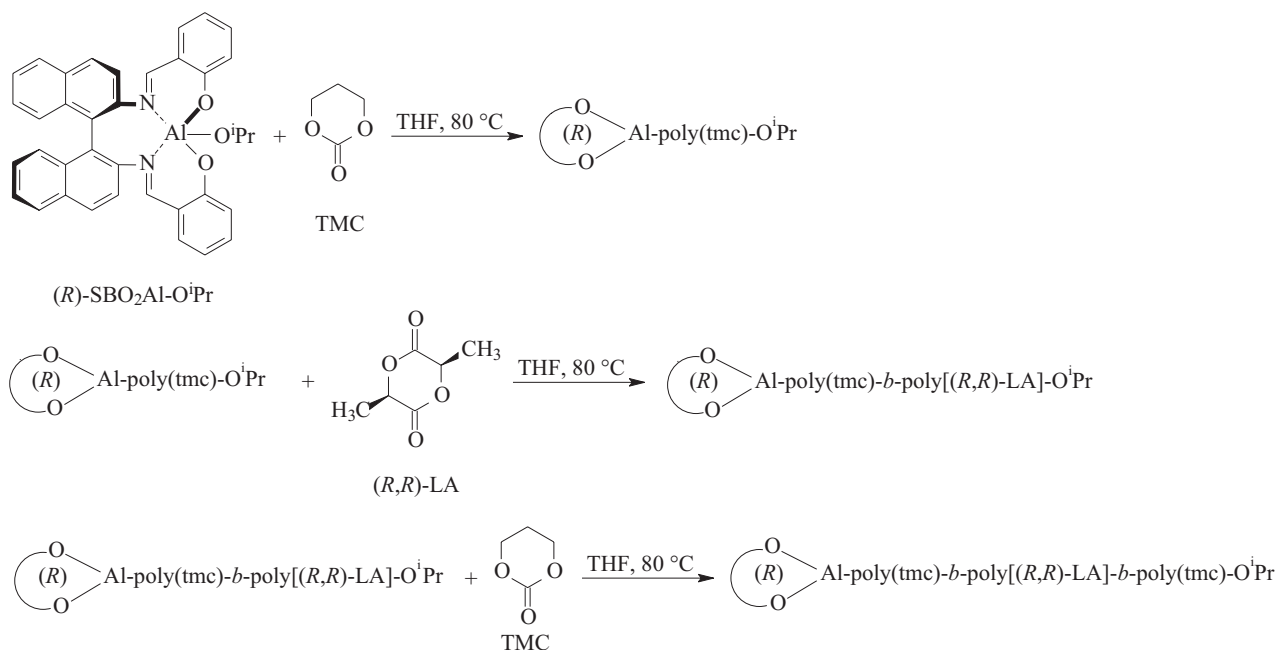
rality on the rate of polymerization of chiral monomers have also shown how to prevent transesterification when bulky catalyst (not necessarily chiral one) is applied. The bulky catalysts are slowing down the rate of transesterification, not changing the rate of propagation.

STEREOCOMPLEXES FROM TRIBLOCK COPOLYMERS

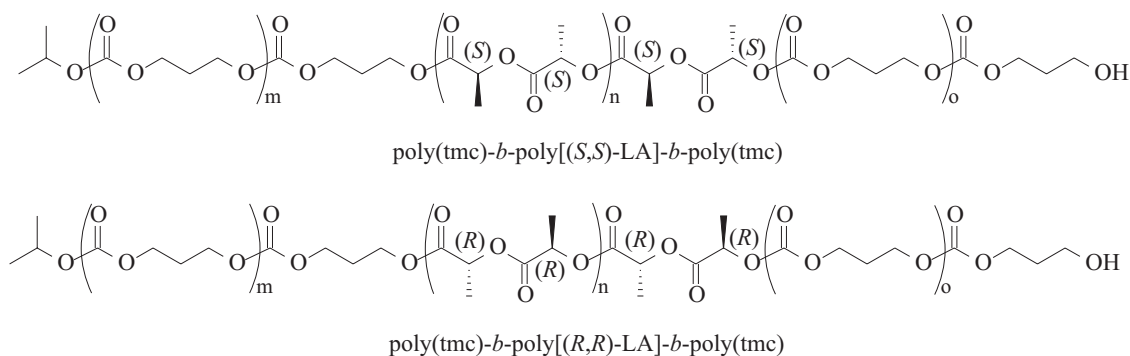
The next idea, related to the previously prepared stereocomplexes of diblock copolymers, pointed to the synthesis of triblock copolymers with chiral blocks, poly[*(S,S)*-LA] in one and poly[*(R,R)*-LA] in the other one. It has been done in the work of copolymerization of lactides with cyclic carbonate [12], in the following way: first a cyclic carbonate, namely trimethylene carbonate (TMC) was polymerized with (*S*)-SBO₂Al-OⁱPr catalyst and after TMC polymerization was completed (*S,S*)-LA was added. When, in turn, its polymerization was completed, again TMC monomer was added to this diblock, and triblock resulted. In the identical way triblock copolymer with (*R,R*)-LA was prepared, namely poly(tmc)-*b*-poly[*(R,R)*-LA]-*b*-poly(tmc). Like the previous works this one was conducted at the high-vacuum systems with using break seals. This tech-



Scheme N. Schematic picture given by Nomura, explaining influence of steric hindrance on the rates in copolymerization of two monomers, namely (*S,S*)-LA and CL, differing in steric structures [11]



Scheme O. Synthesis of triblock copolymer prepared in sequential copolymerization of TMC, (*R,R*)-LA and TMC initiated with (*R*)-SBO₂Al-OⁱPr; in the same way triblock with poly(*S,S*)-LA central block was prepared



Scheme P. Stereocomplex of enantiomeric polylactide blocks in poly(tmc)-*b*-poly[(*S,S*)-LA]-*b*-poly(tmc) and poly(tmc)-*b*-poly[(*R,R*)-LA]-*b*-poly(tmc)

nique allowed triblock copolymers with high purity to be prepared.

This sequence of reactions is illustrated in Scheme O.

When these triblock copolymers have been mixed in solution the corresponding stereocomplex was formed. Its schematic structure is given in Scheme P.

Further studies by DSC allowed determination of the thermal properties of these structurally novel stereocomplexes.

KINETICS OF AGGREGATION IN THE CHAIN GROWTH BY RING-OPENING POLYMERIZATION

As it usually happens when the relatively large research groups decide to solve problems, like fragments of the theory of ring-opening polymerization, then there are various contributions of the members of such a group to the planning, realization and the final result. Sometimes, as shown above, it is exclusively contribution of one leader that has got an idea and with consent of other members of the group is solving a problem "alone", with a help of, *e.g.*, the Ph. D. candidates. In our group it also happened, that Andrzej contributed to investigations of problems, when, although being a *spiritus movens* cooperated with others. We are discussing below, in some details, only one of such a problem. It is so chosen, since it is the most general one not only for the polymer chemistry, but for the reaction kinetics in general.

When studying polymerization of CL with various R_2AlOR' catalysts (I) we observed, that at their low starting concentrations, *i.e.*, low total concentration of the active centers P^* (since polymerization had been shown to be living/controlled, thus $[I]_0 = [P^*]$) – rate of polymerization (r_p) is proportional to $[I]_0$ with a slope equal to one. When $\ln r_p$ was plotted as a function of $\ln [I]_0$, then, from a linear part, with slope equal to 1 (one) the line is converted, after an intermediate period, to the new linear part, with a different slope, approaching 1/2 or 1/3, depending on the size of substituent R in R_2AlOR' ; 1/2 for $[(CH_3)_2CHCH_2]_2AlOCH_3$ and to 1/3 for $(C_2H_5)_2AlOCH_2-CH=CH_2$. Such a behavior is typical for existence of the equilibrium of active species (unimers) with inactivated species, due to their aggrega-

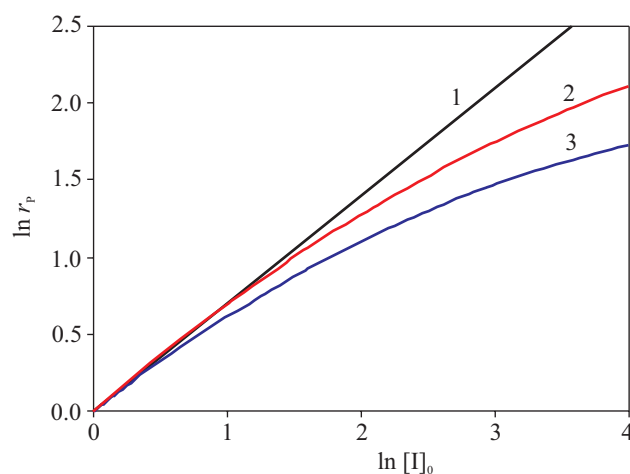
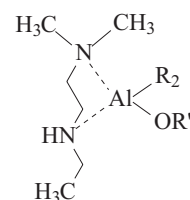


Fig. 5. Dependence of $\ln r_p$ on $\ln [I]_0$ in polymerization of CL catalyzed by R_2AlOR' : 1 – $(C_2H_5)_2AlOCH_2-CH=CH_2$, complexed with $(CH_3)_2NCH_2CH_2NHCH_2CH_3$, 2 – $[(CH_3)_2CHCH_2]_2AlOCH_3$, 3 – $(C_2H_5)_2AlOCH_2-CH=CH_2$

tion. The slightly modified plots are taken from the original data, published in the corresponding paper [13] and are shown in Fig. 5.

When initiator is complexed with a bulky ligand $(CH_3)_2NCH_2CH_2NHCH_2CH_3$ (Scheme R) then there is no aggregation, and linearity of the plot is retained with unchanged slope at the higher concentrations. The larger is the substituents R, the lower the aggregation number.

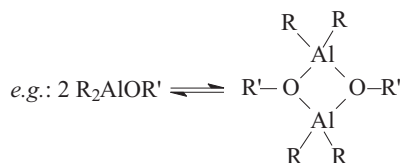


Scheme R. A plausible structure of R_2AlOR' complexed with $(CH_3)_2NCH_2CH_2NHCH_2CH_3$

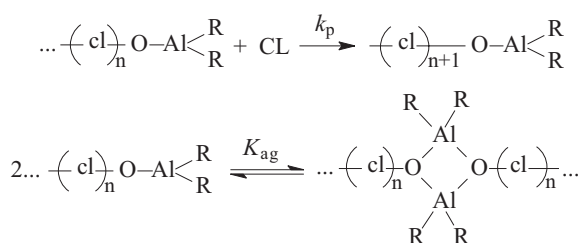
It has to be noted, that in catalyst R_2AlOR' the R-Al bonds are inactive and polymerization takes place on the Al-OR' bond. Thus, the R substituents are present at the

growing, active chain end, whereas R' becomes a part of the other polymer chain end.

Observation of the 1/2 and 1/3 dependence means, that there are the corresponding dimeric and trimeric inactive aggregates in equilibrium with active unimers (Scheme S). The kinetic scheme for such a process is given in Scheme T and general description in Scheme U.

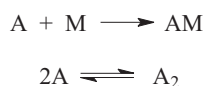


Scheme S. An equilibrium between inactive aggregates (dimeric) and active unimers



Scheme T. Kinetic scheme of polymerization involving reversible aggregation of active centers; aggregated macromolecules are inactive (most probably are not of the same size)

Aggregation may take place for any chemical process, not necessarily polymerization and can be presented in the following general scheme.



Scheme U. General kinetic scheme for reactions with reversible, temporary deactivation, due to aggregation; it could be aggregated dimer (as shown) or any other (higher) aggregate

It was surprising to find out that in spite of the existence of numerous kinetic schemes having analytic solutions, this one did not have solution allowing determination of the rate constant and equilibrium (aggregation/deaggregation) constant directly from the measurements of the rates of reaction. The derivation of the analytical equation is given in [14] and discussed in further details in [15].

The complete derivation is rather cumbersome, but the final form gives access to both rate constant of reaction (k_p) and equilibrium constant (K_{ag}) [Eq. (1)] [14].

$$r_p^{1-m} = -m / (K_{ag} \cdot k_p^{m-1}) + k_p [I]_0 \cdot r_p^{-m} \quad (1)$$

Thus, plotting r_p^{1-m} as a function of $[I]_0 \cdot r_p^{-m}$ (m is either known or found by the trial and error method, until straight line results, r_p is the rate of reaction).

The aggregation number m can also be determined from the following dependence given in Eq. (2) by plotting the $\log r_p$ as a function of $[I]_0$.

$$\log r_p = \log \{k_p (K_{ag}/m)^{1/m}\} + (1/m) \log [I]_0 \quad (2)$$

Application of Eq. (1) gave the values of k_p , being independent on R substituents. It was also found to be approx. 10^2 times lower than k_p for the anionic polymerization [15].

The derived Eq. (1) was successfully used in analysis of other Authors data, studying polymerizations with aggregation. The pertinent rate constants and equilibrium constants were previously calculated by numerical methods. Application of Eq. (1) to these published results have shown a very good agreement between the published data with numerical treatment and application of analytical approach. These included papers by van Beylen and Smets on anionic polymerization of *o*-methoxystyrene [16], by Mueller on anionic polymerization of methylmethacrylate [17], by Kazanski on anionic polymerization of oxirane [18], and by Wilczek and Kennedy on anionic polymerization of hexamethyltrisiloxane [19]. This shows the power and versatility of this approach and elaborated equations.

CONCLUSIONS

In this short review the major personal achievements of Professor Andrzej Duda are described in some details. It has been the first observation of the influence of chirality of the catalyst on the rate of polymerization of a chiral monomer. Then, such an influence allows moderating the rate in copolymerization and changing the rate of one of the comonomers and preparing these ways copolymers with required structure. The second problem presented is related to analytical solution of the general kinetic situation, when reactive species (unimers) are in equilibrium with aggregated species, and when aggregated, then are becoming nonreactive. The solution for such a system was used to treat analytically several polymerization systems, studied numerically by other authors. It has been shown that the developed equations give access to the aggregation number, rate constant and equilibrium constant of aggregation/deaggregation.

These are just two areas of major contributions of Professor Duda. It has to be added, that one has to remember his role in solving several other problems, as it follows from attached bibliography, namely determination of the thermodynamic polymerization parameters of cyclic esters (including lactide), establishing mechanism of ring-opening polymerization with $\text{Sn}(\text{Oct})_2$ catalyst, the most often used in polymerization of lactides and ϵ -caprolactone [20–23]. From the earliest time of his work, just two years after Andrzej joined the Centre, comes also several papers on sulfur polymerization, starting from a paper published in 1978 in *Nature* [24].

Andrzej has published over 100 papers altogether, only very few ones are described in the present Review. The complete bibliography is given below. It has to be noted, that Andrzej has an impressive number of citations for one statistical paper, namely 45. He coauthored five pa-

pers that have been cited over 200 times and a paper cited over 300 times. This is a research paper.

We regret that he has left us closely to the peak of his prominent contributions to the Polymer Science. We regret it even more, since in his capacity of the Chairman of the Polymer Chemistry Department, Professor Andrzej Duda used to be close friend of us, ready to help, whoever and when needed to be helped.

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