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Ring opening polymerization initiated by methylaluminoxane/$AlMe_3$ complexes

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Abstract

The ROP of cyclic ethers, carbonates and esters in the presence of commercially available methylaluminoxane/trimethylaluminum system has been studied. MALDI-ToF end groups analysis indicates that in a majority of systems considered, the polymerization process is initiated by insertion of a monomer into the Al–O–Al bond, generating alkoxide species, which are active sites in coordination polymerization. The polymerization of six-membered carbonates proceeds selectively, forming linear polydiols with high yields at moderate temperatures. The polymerization of oxiranes and lactones is, however, accompanied by back-biting reactions leading to cyclic oligomers. The interaction of oxirane with aluminoxane electrophilic sites causes also the formation of cationic species, which initiate the polymerization of THF. The cationic species formed in those systems were trapped by triphenylphosphine and identified by ^{31}P NMR spectra.

Keywords: Ring opening polymerization; Heterocyclic monomers; Methylaluminoxane

1. Introduction

Alkyl-substituted aluminoxanes were extensively studied in the 1960s as active catalysts in the polymerization of epoxides [1–10]. According to the mechanism proposed by Vandenberg [1,5,8], the chain growth proceeds via alkoxide active centers and is catalyzed by two aluminum atoms linked with an oxygen bridge (Scheme 1).

In later years alkylaluminoxanes were scarcely used in the polymerization of aldehydes [11,12], oxetane [13,14], cyclic esters [10,15–21] and cyclic carbonates [22–24], in the copolymerization of carbon dioxide with oxiranes [25] and oxetane [26], as well as in the copolymerization of olefins or styrene with acrylic monomers [27]. However, these reactions did not find wider practical application due to the high cost of catalysts and problems with the obtaining of aluminoxanes of reproducible structure and activity.

Renewed interest in aluminoxanes was generated in the 1980s as a consequence of the pioneering work of Kaminsky and coworkers [28–31], who found the methylaluminoxane (MAO) to be a highly active cocatalyst for the polymerization of olefins, using group 4 metallocene catalysts [32–34]. Subsequently, much research has been done that makes this cocatalyst industrially feasible. In order to obtain reagents of reproducible activity, commercial MAO solutions are prepared by the reaction of water with a controlled excess of trialkylaluminum, such that the resulting products are composed of $[Al(Me)O]_n$ oligomers, with n ranging from 4 to 30, and residual $AlMe_3$. The typical Me/Al ratio in these products is in the range 1.6–2.0 [35]. The question of the structure of MAO has not been solved due to the fact that it is not possible to isolate crystalline samples. DFT calculations suggest that MAO oligomers may exist as an equilibrium between several cage structures containing Al_2O_2 rings with the hexagonal-faced $[Al(Me)O]_{12}$ being the most abundant for a temperature range of -75 to $+325$ °C. In the real system MAO and $AlMe_3$ exist as free and bound species according to Scheme 2.

In metallocene catalyzed polymerization a considerable excess of the organoaluminum compound is used in relation to the transition metal derivatives (500–10,000 fold excess) in order to achieve a high concentration of active centers and protect them against impurities. These compounds remain in the system after completion of the unsaturated hydrocarbons polymerization and can be used in situ as initiators of polymerization of acrylic and heterocyclic monomers, to produce polymer blends in a one batch procedure [36]. Such a possibility prompted us to a more detailed study of

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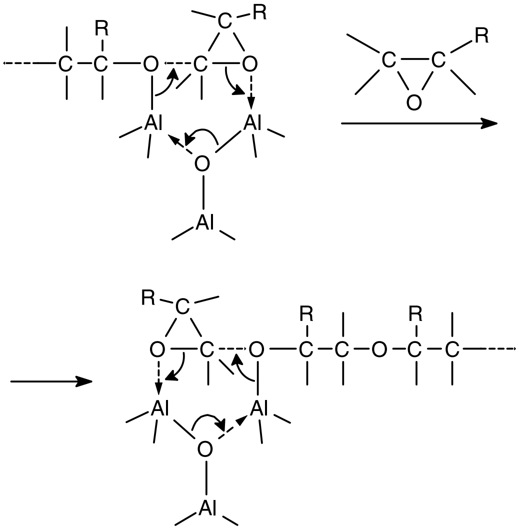


Scheme 1.

$$[Al(Me)O]_n + m/2\ (AlMe_3)_2 \rightleftharpoons$$
$$\rightleftharpoons [Al(Me)O]_n \times (AlMe_3)_m \rightleftharpoons$$
$$\rightleftharpoons Me_2AlO[Al(Me)O]_{n-1}AlMe_2 \times (AlMe_3)_{m-1}$$

Scheme 2.

the mechanisms of polymerization of heterocyclic monomers initiated in the presence of commercial MAO/$AlMe_3$ samples. The main purpose of this work was to get acquainted with the possibilities of applying these systems to generate cationic or covalent (pseudoanionic) centers in the polymerization of cyclic ethers, esters and carbonates.

2. Experimental section

2.1. Materials

All materials were purified, stored and used in dry nitrogen atmosphere. Toluene (POCh), tetrahydrofuran (THF) (POCh) and hexane (Merck) were fractionally distilled from sodium/-potassium and benzophenone after color change to navy blue, and then stored over dried 4 Å molecular sieves. Propylene oxide (PO) (Merck) was dried with CaH_2 and fractionally distilled on dried 4 Å molecular sieves. ε-Caprolactone (CL) (Aldrich) and δ-valerolactone (VL) (Aldrich) were dried with CaH_2 and distilled under reduced pressure on dried 5 Å molecular sieves. Triphenylphosphine (Aldrich) was crystallized from dry hexane, then dried under vacuum for 1 day and used as a toluene solution. Diethyl ether was shaken with an aqueous solution of ferrous sulfate/H_2SO_4, then washed with water, dried with $CaCl_2$, filtered and distilled from sodium onto 5 Å molecular sieves. Ethylene carbonate (EC) (Aldrich) was dried over P_4O_{10}, then fractionally distilled under reduced pressure and crystallized from dry methylene chloride. Methylene chloride (POCh) was fractionally distilled from CaH_2 onto dried 4 Å molecular sieves. Propane-1,3-diol and 2,2-dimethylpropane-1,3-diol were distilled under reduced pressure. 3,6-Dimethyl-1,4-dioxane-2,5-dione (*rac*-lactide, LA) (Aldrich) was crystallized from a mixture of dry toluene and dried at 30 °C under vacuum (for homopolymerizations) or used as supplied without further purification (for copolymerizations). Ethylene oxide (EO) (Fluka), and diethyl carbonate (Aldrich) were used as supplied without further purification. Tin(II) 2-ethylhexanoate (Aldrich) was used as supplied. Organometallic compounds: trimethylaluminum (2.0 M in toluene, Aldrich) and MAO (10% by weight in toluene, Aldrich, analyzed: Al/–CH_3 ratio of 1.9) were used directly from Sure/Seal™ bottles.

2.2. Procedures

Trimethylene carbonate (TMC) and neopentyl carbonate (NPC) were synthesized in the reaction of equimolar quantities of diethyl carbonate and propane-1,3-diol or 2,2-dimethylpropane-1,3-diol, respectively, in the presence of tin(II) 2-ethylhexanoate as catalyst at 160 °C during 8 h. Then, ethanol and unreacted substances were evaporated under reduced pressure. The obtained polycarbonates were thermally decomposed, then the monomers were crystallized from a mixture of dry benzene/tetrahydrofuran (1:4) and dried at 30 °C under vacuum.

The polymerizations were carried out in glass pressure ampoules sealed by a screw with gasket on coupling, in dry nitrogen atmosphere. Solid monomers were placed in ampoules in a nitrogen stream using glass adapters. Liquids, such as monomers or their solutions as well as solvents were added by glass syringes. Gaseous EO was condensed in a cooled ampoule. Organometallic compounds solutions were added using glass syringes a few minutes after the ampoule was placed in an acetone/dry-ice cooling bath. The amount of MAO/$AlMe_3$ used for the polymerizations was equal to 1.33 mL of 10% MAO solution. After addition of all the components, the ampoule was placed in an oil or water bath at an appropriate temperature. After desired time the ampoule was cooled, degassed, opened and methylene chloride was added in order to dissolve the products. The solution was shaken once with diluted hydrochloric acid to wash out the catalyst residue. Then, the organic phase was washed with water three times and dropped into stirred methanol to precipitate the polymers (or the whole was subjected to evaporation when nothing precipitated). The products were dried under vacuum at 50 °C for 2 days. The yields of ester and carbonate homo- and copolymers were calculated from the masses of methanol non-soluble fractions.

2.3. Analyses

Relative molecular mass and molecular mass distribution were determined by MALDI-ToF or GPC techniques. MALDI-ToF spectra were measured in linear mode on a Kompact MALDI 4 by Kratos analytical spectrometer using a nitrogen gas laser ($\lambda = 337$ nm) with 2,5-dihydroxybenzoic acid (DHB) or 2-[(4-hydroxyphenyl)diazenyl] benzoic acid (HABA) as a matrix. Gel permeation chromatograph (RI detection) was equipped with a Jordi gel DVB column, Lab Alliance isocratic pump (1 mL/min), SFD refractive index detector RI-2000F and Degasys degasser DG-2410. GPC analyses were carried out in THF or toluene as a solvent at 20 °C. The relative molecular masses were determined with polystyrene standard calibration. The relative molecular mass and dispersity of the polytetrahydrofuran sample (Table 2, entry 5) were determined in the Institute of Coal Chemistry PAS, Gliwice using a GPC system with multiangle light scattering detector DAWN-EOS of Wyatt Technologies and differential refractive index detector Δn-1000 RI WGE Dr Bures. Polymer standard service (PSS) SDV 1×105 Å $+1\times 103$ Å $+2\times 102$ Å columns were used. Measurements were performed in THF at 30 °C with a nominal flow rate of 1 mL/min. Results were evaluated using the ASTRA software from Wyatt Technologies. Refractive index increment for polytetrahydrofuran in THF was assumed as 0.062 mL/g [37]. Nuclear magnetic resonance spectra were registered by Varian Mercury spectrometer; ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{31}P NMR (162 MHz) in $CDCl_3$ or C_6D_6 as solvents at room temperature.

3. Results and discussion

3.1. Polymerization of PO

The PO polymerizations in the presence of the MAO/$AlMe_3$ system were carried out at aluminum to monomer mole ratio of 1:25 at 20–60 °C. On the basis of the MALDI-ToF spectra of the products obtained it can be found that oligoetherodiols of M_n in the range 900–1500 and $M_w/M_n \approx 1.1$ are the main reaction products (75–88% of total population) (Fig. 1(a), Table 1). Signals of the second population of M_n 400–700 are also present in the spectra, which may be attributed either to the linear chain terminated by CH_2=CH–CH_2–O and OH group (products of transfer reaction) or to cyclic ethers. In our opinion, this second assignment is much more probable, since in ^{1}H NMR spectra no signals characteristic of vinyl group protons are observed.

The formation of cyclic products is a characteristic feature of oxirane cationic polymerizations, which are accompanied by back-biting type reactions [38].

In order to confirm the hypothesis of the formation of cationic active species, the polymerization was interrupted by the addition of triphenylphosphine to the system, which is a very efficient trap of cationic active centers generated in the polymerization of heterocyclic monomers (Scheme 3) [39].

The ^{31}P NMR spectra of isolated products of PO polymerization in the presence of MAO (Fig. 2(b)) and also of the reaction mixture (which are not shown here) contain a characteristic signal at $\delta = 23.35$ ppm, which lies in the range typical for phosphonium cations formed in the trapping of cationic active species.

The cationic active centers generation can be presented by the following scheme (Scheme 4). In the first step, the oxirane molecules form a complex with the strongly electrophilic aluminum atom in the aluminoxanes structures. In a subsequent step, the oxirane ring opening takes place resulting from the nucleophilic attack of the free oxirane molecule on the complexed one with the formation of an onium ion and oligomeric counterion.

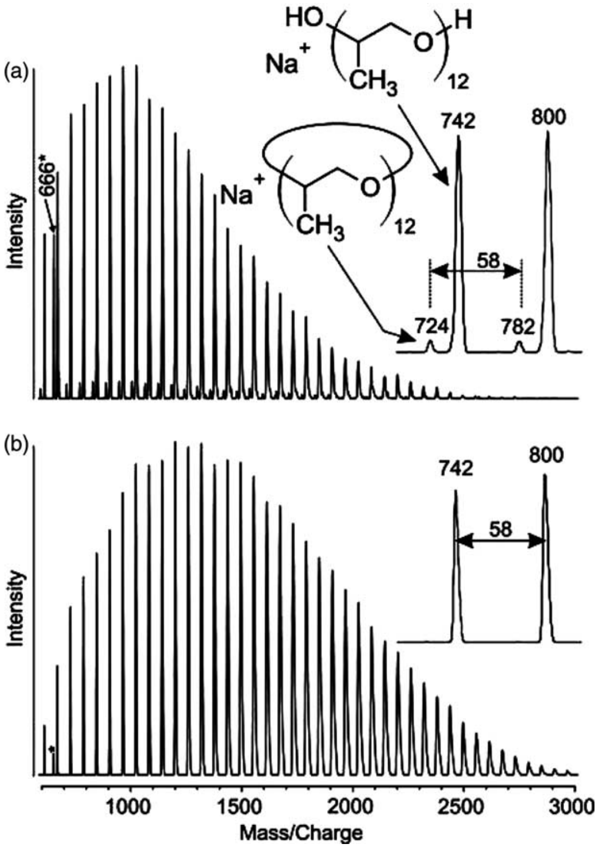


Fig. 1. MALDI-ToF spectra of the products of propylene oxide polymerization in the presence of (a) MAO/$AlMe_3$ and (b) MAO heavy phase (Table 1, entries 1 and 6, respectively). *The peaks of 666 mass/charge value are the superposition of the matrix and product signals (a) or matrix signal (b).

From the work of Sinn et al. [35] it is known that toluene solutions of MAO–$AlMe_3$ cocatalysts produced under well defined conditions show a phase separation if diethyl ether is added. The lower heavy phase with a high density of about 0.95 g/mL shows a ratio CH_3–/Al = 1.5 and a low ether-content of only 3.6%. On the basis of elemental analysis and cryoscopic studies it was suggested that a mixture of oligomers of general formula $[Al_{16}O_{12}(CH_3)_{24}]$ is the main component of this phase. When using this fraction for the initiation of PO polymerization we obtained exclusively products of a linear structure (Fig. 1(b)), which might suggest that this part of catalysts acts as a coordination (pseudoanionic) catalyst according to the Vanderberg type mechanism (Scheme 1) rather than a cationic initiator. The presence of two hydroxyl groups in the obtained products let us assume that prior to hydrolysis O–Al bonds occur on both ends of the chain. This is probably connected with the cleavage of the Al–O–Al bond system at the initiation step (Scheme 5).

The phase separation brings MAO/$AlMe_3$ oligomers along with $Al(CH_3)_3$ diethyl etherate into the upper-phase [35]. The presence of excess $AlMe_3$ in this phase is explicitly confirmed by the ^{1}H NMR spectra (Fig. 3(b)), in which in the δ range from 0.15 to -0.65 ppm, a sharp signal of the complex Me–Al

Table 1
Homopolymerization of propylene oxide (PO) initiated by MAO-based catalytic systems

Entry	Catalytic system (molar ratio)	Time (h)	Temperature (°C)	Yield (wt%)	Oligodiols (linear)[a]			Macrocycles[a]		
					(mol%)	M_n	M_w/M_n	(mol%)	M_n	M_w/M_n
1	MAO[b,c]	72	20	65	88	1170	1.1	12	650	1.4
2		24	40	74	87	900	1.1	13	700	1.1
3		24	60	84	75	1000	1.1	25	700	1.1
4	MAO[b]/$AlMe_3$ (1:1)[c]	70	20	63	84	1070	1.1	16	650	1.3
5	MAO upper phase[d]	70	20	65	63	1350	1.1	37	410	1.1
6	MAO heavy phase[d]	70	20	48	100	1550	1.1	0[e]	–	–

In bulk.

[a] Analysis of oligodiols and macrocycles from MALDI-ToF spectra.

[b] Commercial methylaluminoxane (MAO/$AlMe_3$); the amount of MAO/$AlMe_3$ used for the polymerizations was equal to 1.33 mL of 10% MAO solution.

[c] PO/MAO molar ratio of 25.

[d] Separated according to Sinn's procedure [35], PO to commercial MAO before separation ratio of 25.

[e] No polymerization product was obtained.

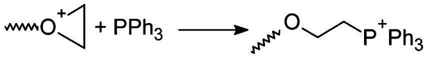
group protons occurs within a broad signal attributable to protons present in the oligomers. The use of this fraction as a catalyst of PO polymerization leads to the formation of products of higher macrocycle content than that in the reaction products involving a starting MAO/$AlMe_3$ mixture (Table 1, entry 5). Therefore, it can be assumed that a certain excess of $AlMe_3$ favors the generation of electrophilic centers in MAO/$AlMe_3$ complexes capable of cationic initiation of oxirane polymerization.

The coordination of the oxirane molecule and attack of the nucleophilic agent may, therefore, lead both to coordination polymerization (Scheme 5) and cationic polymerization (Scheme 4). The reaction course depends probably on the nucleophilic properties of the oxygen atom in the Al–O–Al bond system. If the oxygen atom is bound only with two aluminum atoms, then its nucleophilicity is much greater than that of the monomers and coordination polymerization is initiated. The oxygen atoms coordinated with the third aluminum atom resulting from the aluminoxanes association or complex formation with $AlMe_3$ weakens the nucleophilic properties of the initiator and favors the attack of monomers onto the activated oxirane molecule.

The monomer activation by excess aluminum trialkyl is probably of no essential importance for the generation of active species, since neat $AlMe_3$ does not initiate the oxirane polymerization and introduction of an additional amount of this compound to the starting reagent only slightly increases the macrocycle fraction content (Table 1, entry 4).

3.2. Copolymerization of PO with THF

The MAO/$AlMe_3$ system does not initiate the polymerization of THF. However, the introduction to the system of a small amount of PO as coinitiator (0.2–1.0 mol% with respect to THF) permits to obtain high molecular weight polyethers, which, as results from the analysis of ^{1}H NMR spectra (Fig. 4(a)) contain over 99 mol% of THF monomeric units (Table 2).



Scheme 3.

After the addition of triphenylphosphine, two signals of phosphonium cations are observed in the ^{31}P NMR spectrum (Fig. 2(c)). One of them is characteristic of phosphonium cations containing PO m.u. (δ 23.30 ppm), and the second more intensive one at δ 24.08 ppm comes from phosphine adducts with chains terminated by THF m.u.

GPC traces (both RI and LS signals) of the polymers of high THF m.u. content show a monomodal distribution of molecular masses. At the lowest catalyst to PO molar ratio (Al/THF 1:200, PO/THF 1:500) the number average molecular mass M_n (determined by GPC with light scattering detection) was 21,000 ($\pm$3%) and dispersity M_w/M_n was 1.5 (Fig. 5). This means that at an average, about 300 THF m.u. and 2–3 oxirane m.u. occur in one chain. When assuming that no chain transfer reactions proceed in this system (which in the case of THF polymerization is very probable), it can be estimated that one active center falls at an average per 3.4 aluminum atoms

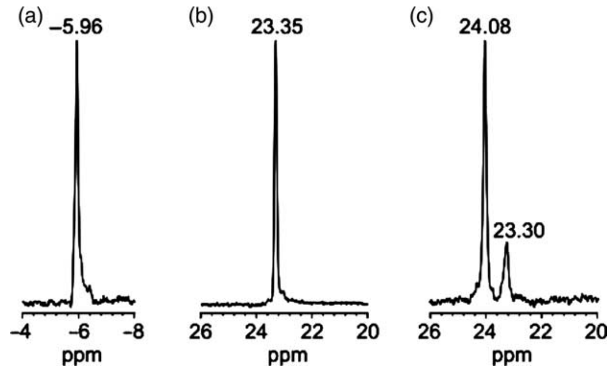
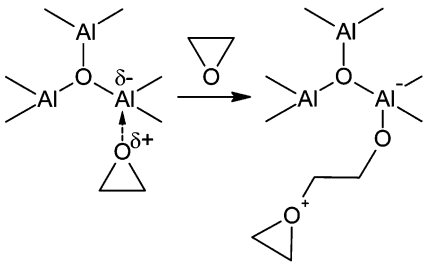
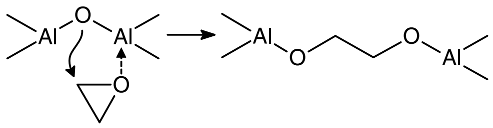


Fig. 2. Fragments of ^{31}P NMR spectra of (a) triphenylphosphine, (b) adduct of triphenylphosphine and the product of propylene oxide polymerization in the presence of MAO/$AlMe_3$, (c) adduct of triphenylphosphine and the product of THF and propylene oxide copolymerization at the mole ratio 100:1 in the presence of MAO/$AlMe_3$ ($CDCl_3$).



Scheme 4.



Scheme 5.

involved in the formation of counterions. It is interesting to note that in the presence of THF the polymerization proceeds also when using the 'heavy phase' of MAO/$AlMe_3$ (Table 2, entry 4) which does not generate cationic species in PO polymerization. The reason for this is probably the dissociation of $[Al_{16}O_{12}(CH_3)_{24}]$ cages under the influence of THF [40].

Zurek et al. examined the interaction of THF with $AlMe_3$, $[Al(Me)O]_6$ cage and $[Al(Me)O]_6 \times AlMe_3$ complex. The coordination of one THF molecule was found to be exothermic by −14.17, −6.56 and −23.15 kcal/mol, respectively [41]. Consideration of these data leads to a conclusion that Lewis acidity of electrophilic centers in MAO–$AlMe_3$ might be higher than that in free $AlMe_3$ and MAO species.

The average relative molecular mass of the copolymers decreases with an increase in the PO content in the initial monomer feed (Table 2). At a 1:1 monomer mole ratio, a copolymer of composition similar to equimolar and bimodal mass distribution (M_n 9.5×10^3 and 0.9×10^3) is obtained.

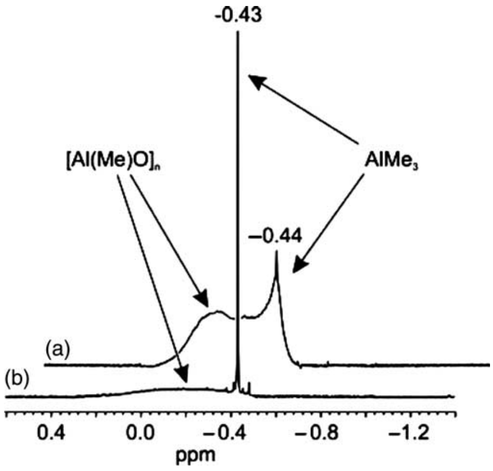


Fig. 3. Fragments of ^1H NMR spectra of Al–CH_3 protons in (a) MAO heavy phase and (b) MAO upper phase.

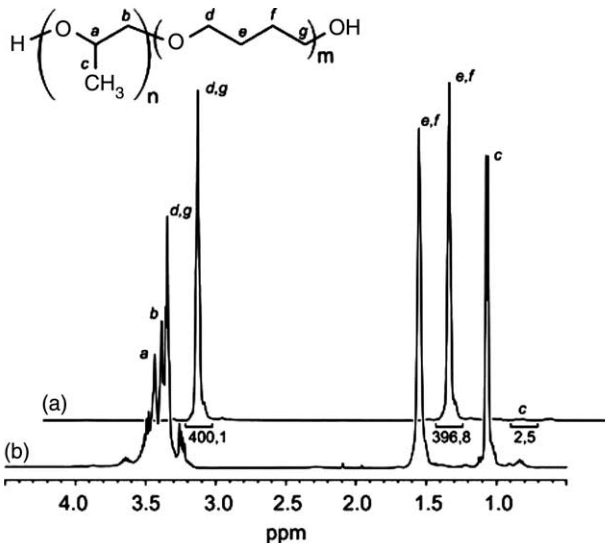


Fig. 4. ^1H NMR spectra of the copolymerization products of THF and propylene oxide at the mole ratio (a) 500:1, (b) 1:1 in the presence of MAO/$AlMe_3$ (Table 2, entries 5 and 7, respectively).

3.3. Polymerization of cyclic esters

Two six-membered esters (VL and LA) were used for the studies as well as a seven-membered monomer (CL). To obtain oligomeric products suitable for analysis by the MALDI-ToF method, the reactions were carried out at 60–100 °C in the presence of 4 mol% of catalysts. The monomer conversion in a majority of systems exceeded 70% (Table 3). An analysis of MALDI-ToF spectra of the products obtained (Fig. 6) shows that they are a mixture of linear and macrocyclic products.

The linear products are α,ω-hydroxyacids. Therefore, it can be assumed that also cyclic esters undergo insertion into the Al–O–Al bond giving rise to alkoxide type active species and aluminum carboxylate ones that are probably unable to attack the cyclic esters (Scheme 6).

In the MALDI-ToF spectrum (Fig. 6) of lactide oligomers both populations of chains of even and odd number of lactic acid m.u. can be observed. The odd number of acid m.u. shows that under the process conditions the polymer chain undergoes intramolecular transesterification (leading to the formation of macrocycles) and intermolecular transesterification (leading to an exchange of segments), which is a typical phenomenon for the polymerization of lactides in the presence of coordination catalysts comprising Al, Zn or Sn [42,43].

On the other hand, it is known that the CL polymerization in the presence of aluminum dialkylalkoxides proceeds selectively to products of a linear structure and in some systems products of M_n as high as 5×10^5 [44–46] and polydyspersity <1.3 can be obtained. In systems with MAO, even for reactions carried out at room temperature a macrocyclic fraction is formed and the M_w/M_n values for the fractions of linear products are close to 2 (Table 3, entry 5). Therefore, it can be assumed that the electrophilic centers present in MAO/$AlMe_3$ catalyze the transesterification processes.

Table 2
Copolymerization of THF with propylene oxide (PO) initiated by MAO-based catalytic systems

Entry	Monomers (molar ratio)	Catalytic system (molar ratio)	Time (h)	Temperature (°C)	Copolymer				
					Yield (wt%)	Composition (mol%)[a]		$M_n\times10^{-3}$[b]	M_w/M_n[b]
						PO	THF		
1	THF	MAO[c]	24	60	0[d]	–	–	–	–
2	THF/PO (100:1)	MAO[c]	12	20	31	0.9	99.1		
3		MAO upper phase[e]	20	20	8	0.7	99.3		
4		MAO heavy phase[e]	20	20	42	0.8	99.2		
5	THF/PO (500:1)[f]	MAO[c]	65	20	43	0.8	99.2	21.0	1.5
6	(50:1)		24	20	39	2.2	97.8	18.0	1.8
7	(1:1)		48	20	36	48.7	51.3	9.5 [g] 0.9	1.6 1.4

In bulk, monomers/catalyst molar ratio of 50.

[a] Calculated from ^{1}H NMR spectra in $CDCl_3$.

[b] Obtained from GPC in THF.

[c] Commercial methylaluminoxane ($MAO/AlMe_3$); the amount of $MAO/AlMe_3$ used for the polymerizations was equal to 1.33 mL of 10% MAO solution.

[d] No polymerization product obtained.

[e] Separated according to the Sinn's procedure [35], PO to commercial MAO before separation molar ratio of 25.

[f] Monomers/catalyst molar ratio of 200.

[g] Bimodal mass distribution was observed.

It should be noted, however, that polymerization is not killed after the introduction of triphenylphosphine and no signals characteristic of phosphonium cations were observed. This suggests that in the presence of CL, cationic active species are not formed.

To confirm this hypothesis we carried out also attempts to copolymerize THF with CL and PO in the presence of an aluminoxane catalyst. An analysis of NMR spectra (which are not shown here) clearly shows that in this type of ternary systems THF does not incorporate to the growing chain, and CL and PO copolymers are exclusively the reaction products.

3.4. Polymerization of cyclic carbonates

The results of TMC, NPC and EC polymerization at different conditions using 4 mol% of $MAO/AlMe_3$ as catalyst are presented in Table 4.

The polymerization of six-membered carbonates starts at 20 °C practically immediately after mixing the reagents. When carrying out the reaction within 30–60 °C, yields in the 80–95% range are achieved. An analysis of ^{1}H and ^{13}C NMR spectra indicates that the products obtained contain signals characteristic of TMC m.u. and NPC m.u. in the homopolymers [24]. Depending on the reaction conditions, the number-average relative molecular mass fraction which gives signals in MALDI-ToF spectra, are of the order of $2.3–3.5\times10^3$. Fig. 7 shows typical MALDI-ToF spectra of the products obtained. They reveal only the sets of signals corresponding to protonated linear polycarbonates terminated by a hydroxyl chain-end. This indicates that in the polymerization of the studied six-membered cyclic carbonates no back-biting reactions take place and linear products bonded with aluminum atoms from both sides are formed selectively. Tests with the use of triphenylphosphine showed that in the systems studied no cationic active centers, which could be transferred into phosphonium cations, are formed. Therefore, one can assume that the polymerization of TMC and NPC occurs according to a coordinaton (pseudoanionic) mechanism. One of the plausible explanations is shown in Scheme 7.

It includes monomer insertion into the aluminoxane Al–O–Al bond leading to the formation of aluminum alkoxide and carbonate groups followed by propagation on the alkoxide side and final hydrolysis of Al–O bonds accompanied by elimination of a CO_2 molecule from the terminal carbonate unit.

The relative molecular masses of TMC and NPC homopolymers as determined by GPC analysis are significantly higher than those determined by MALDI-ToF. In the case of

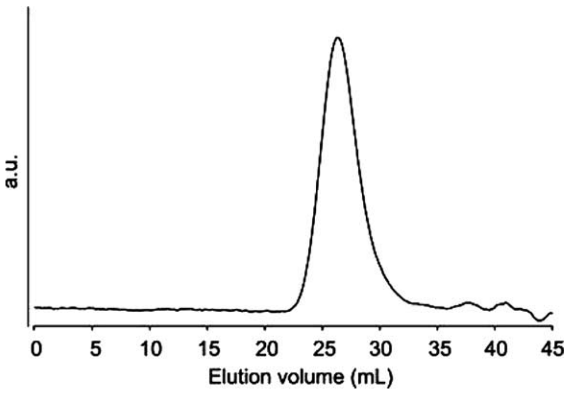


Fig. 5. GPC trace of the copolymerization product of THF and propylene oxide at the mole ratio 500:1 in the presence of $MAO/AlMe_3$ (Table 2, entry 5).

Table 3
Polymerization of δ-valerolactone, *rac*-lactide and ε-caprolactone initiated by MAO/AlMe$_3$

Entry	Monomer	Time (h)	Temperature (°C)	Yield (wt%)	Oligodiols (linear)[a]		Macrocycles[a]	
					%	M_n	%	M_n
1	VL	80	60	84	86	3500	14	1500
2	LA	48	80	40	91[b]		9[b]	1200
					69 (even)[b]	1400		
					22 (odd)[b]	1100		
3		48	100	86				
4	CL	20	60	89	91[c]		9 (Na$^+$)[c]	1600
					13 (Na$^+$)[c]	2900		
					78 (K$^+$)[c]	2900		
5		20	20	70		23,800[d]		~1000[d]

Carried out in toluene as a solvent; monomer/catalyst molar ratio of 25; catalyst: commercial methylaluminoxane (MAO/AlMe$_3$); the amount of MAO/AlMe$_3$ used for the polymerizations was equal to 1.33 mL of 10% MAO solution.

[a] Analysis of oligodiols and macrocycles from MALDI-ToF spectra.

[b] Data of series of even, odd or both number of m.u. per polymer, respectively.

[c] Data of sodium, potassium or both mass series, respectively.

[d] From GPC in toluene.

TMC homopolymers the M_n values depend essentially on the kind of solvent used. When the reactions are carried out in methylene chloride, the M_n values exceed 2×10^5 (Fig. 8(a)), whereas in reactions carried out in toluene these masses are smaller than 10^4. In these latter examples, after a short time the system transforms into the state of a gel, which probably causes a considerable decrease in the propagation rate. However, diffusion to free active centers is possible and the polymerization process is not inhibited. The gelation phenomenon is of no importance in the NPC polymerization and in both solvents products of similar relative molecular masses (ca. 4×10^4 and M_w/M_n in the range 1.5–1.6) are formed.

Very large relative molecular weights of TMC polymers obtained in a homogeneous medium show that under these conditions only a small number of Al–O–Al bonds is transferred into active centers. If another monomer besides TMC is present in the reaction medium, e.g. lactide or ε-caprolactone, then products of a bimodal molecular mass distribution result from the copolymerization (Fig. 8(b)). One of the populations has M_n similar to that of the TMC homopolymer (3–4×10^5), and the second one by one order of magnitude lower (1.0–1.5×10^4).

The copolymers of TMC and CL were subjected to fractionation (by precipitation with methanol from methylene chloride solutions). TMC-rich ($M_n\sim3.1\times10^5$) and CL-rich ($M_n\sim1.5\times10^4$) copolymers were isolated by fractionation.

Fig. 9 shows ^{1}H NMR and fragments of ^{13}C NMR spectra of such fractions formed in the initial polymerization period (the total monomer conversion was ~7%). In both products

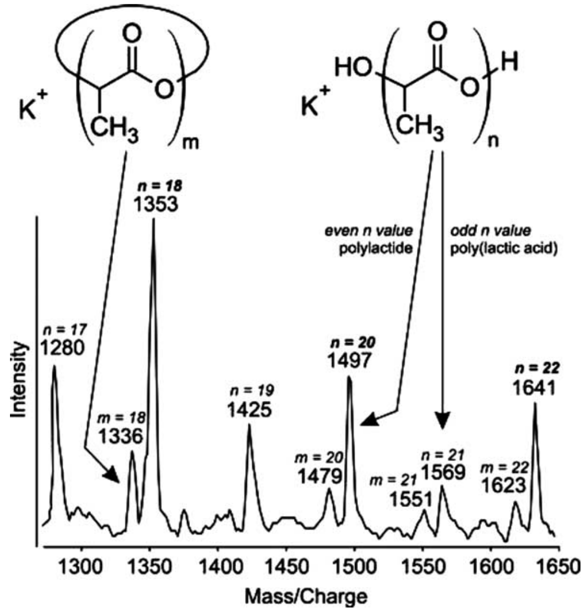
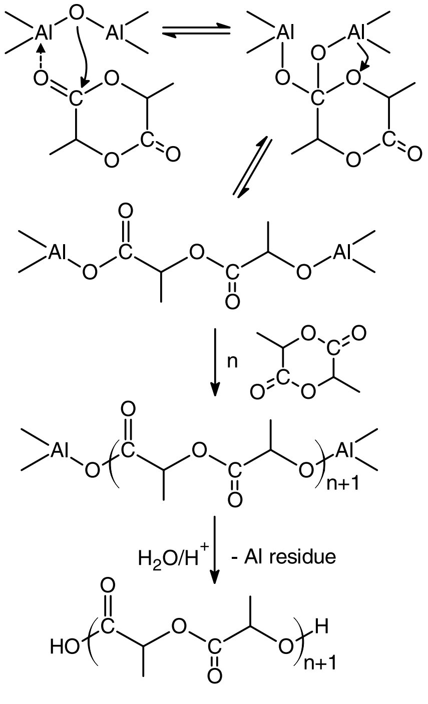


Fig. 6. Fragment of the MALDI-ToF spectrum of the product of *rac*-lactide polymerization in the presence of MAO/AlMe$_3$ (Table 3, entry 2).



Scheme 6.

Table 4
Polymerization and copolymerization of six-membered cyclic carbonates initiated by MAO/$AlMe_3$

Entry	Monomer	Time (h)	Temperature (°C)	Yield (wt%)	M_n[a]	M_w/M_n[a]	Carbonate unit content[b] (mol%)
1	TMC	20	30	82	2350[c]	1.1[c]	
2		20	60	84	8000	1.4	
3		20[d]	20	72	224,000	2.0	
4	TMC+CL (1:1)	3	20	7			65
5		48[d]	60	81	14,700[e]	1.2	51
					314,000	1.5	
6	TMC+LA (1:1)	24	60	64	10,100[e]	1.2	57
					403,000	1.7	
7	NPC	20	30	93	38,300	1.5	
8		20[d]	60	94	45,000	1.6	
9		48	60	92	3500[c]	1.1[c]	

Carried out in toluene as a solvent; monomer/catalyst molar ratio of 25; catalyst: commercial methylaluminoxane (MAO/$AlMe_3$); the amount of MAO/$AlMe_3$ used for the polymerizations was equal to 1.33 mL of 10% MAO solution.

[a] Obtained from GPC in THF.

[b] Calculated from ^1H NMR in $CDCl_3$.

[c] Obtained from MALDI-ToF.

[d] Methylene chloride used as a solvent.

[e] Bimodal distribution.

the signals characteristic for CL–CL–CL or TMC–TMC–TMC homosequences are considerably more intensive than that for triads, in which both m.u. occur. This shows that in the catalyst structure active centers are present which favor the propagation of one of the monomers, and the final polymer structure depends on the concentration of these centers and secondary transesterification reactions. Similar phenomena were earlier observed by Hoecker et al. [47] in ring opening copolymerization of cyclic carbonates and cyclic esters initiated by metal alkoxides.

4. Concluding remarks

The commercially available MAO initiates the polymerization of many types of heterocyclic monomers and in some systems it enables the obtaining of polymers with high yield at room temperature. An exact analysis of the mechanism of active species generation is impossible since the structure of aluminoxane oligomers, which occur in these systems and moreover, can change during polymerization, is not known. An analysis of the end groups by MALDI-ToF indicates, however that in a majority of systems studied, monomer insertion into Al–O–Al bonds occurs. Further chain growth could proceed on alkoxide active centers. Polymeric diols or α,ω-hydroxyacids are the main products, depending on the monomer used. In reactions of MAO and PO, oxonium ions are also generated, which can initiate the cationic polymerization of oxirane and THF. Aluminoxane oligomers form stable anions in this system (which resembles their behavior in metallocene catalyzed polymerization), due to which the obtaining of polyTHF of $M_n > 2 \times 10^4$ is possible. The average number of aluminum atoms necessary for the stabilization of the negative charge in these agglomerates is between 3 and 4. In the PO

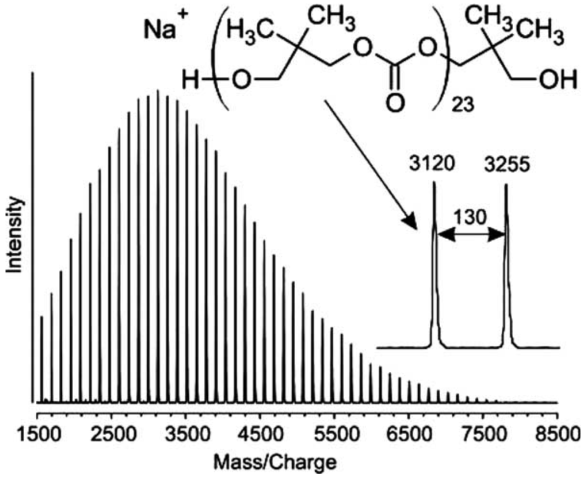
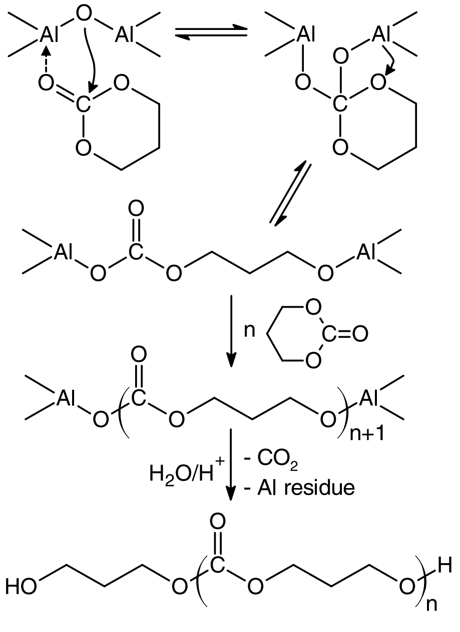


Fig. 7. MALDI-ToF spectra of the product of neopentyl carbonate polymerization in the presence of MAO/$AlMe_3$ (Table 4, entry 6).



Scheme 7.

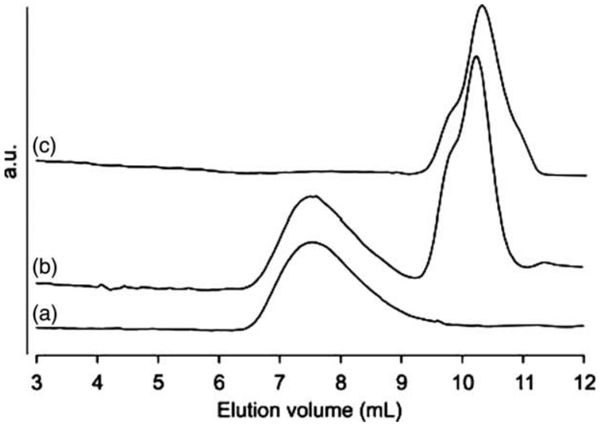


Fig. 8. GPC traces of (a) homopolymerization product of TMC carried out in the presence of MAO/$AlMe_3$ in CH_2Cl_2 (Table 4, entry 3), (b) product of TMC and CL copolymerization carried out in the presence of MAO/$AlMe_3$ in toluene (Table 4, entry 5), (c) fraction of (b) soluble in methanol–methylene chloride solvents system.

homopolymerization, the cationic processes can be completely eliminated, providing the initiator is deprived of the excess of $AlMe_3$. Under these conditions the reaction proceeds selectively according to the coordination mechanism with the formation of linear products. The cationic active centers are not generated in the polymerization of cyclic esters and cyclic carbonates.

The coordination polymerization of cyclic esters in the presence of MAO does not, however, show hopes for practical application, since it is accompanied by back biting reactions leading to macrocyclic side products. This phenomenon is not observed in the polymerization of six-membered cyclic carbonates and as results from preliminary observations, in homogeneous systems it is possible to obtain polycarbonatodiols of M_n exceeding 10^5. It seems that after appropriate optimization of the polymerization conditions, MAO can be considered as an alternative for the hitherto solutions. However, the achieving of precise control of the relative molecular weight distribution will be an essential problem, since quantitative initiation in systems with strongly associated systems of Al–O–Al bonds, is of little probability and the active centers are generated in succession during polymerization. At high relative molecular weights of polycarbonates, the M_w/M_n values are greater than 1.5. Also oligocarbonatodiols of $M_n < 10^4$, which can be formed in heterogeneous systems due to the fact that the propagation is controlled by diffusion, can be interesting products useful for the production of polyurethanes.

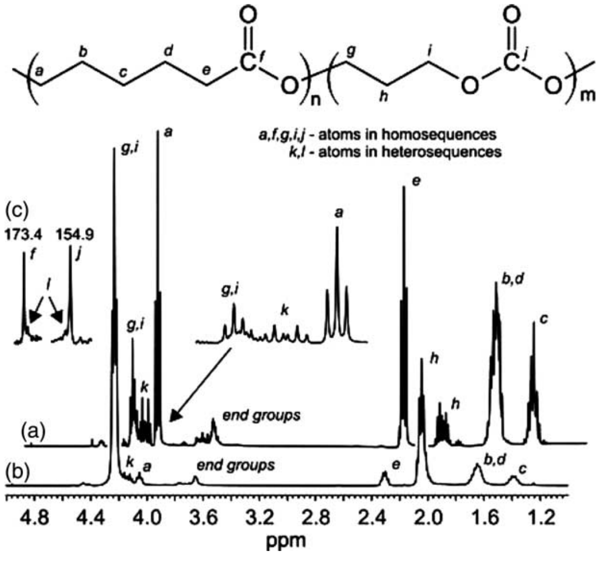


Fig. 9. ^1H NMR spectra of (a) ε-caprolactone-rich (91 mol%) and (b) trimethylene carbonate-rich (93 mol%) fractions and (c) fragments of ^{13}C NMR spectra of the product of trimethylene carbonate copolymerization with ε-caprolactone in the presence of MAO/$AlMe_3$ (Table 4, entry 4).

Acknowledgements

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