Propylene Oxide Copolymerization with Carbon Dioxide using Sterically Hindered Aluminum Catalysts

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Highly active, new bis(2,6-di- tert-butyl-4-methyl-phenoxy)aluminum methylphosphonate sterically hindered aluminum catalyst was developed for both, homo- and copolymerization of propylene oxide with carbon dioxide. The behaviour of this catalyst compared with that of bis(2,6-di-tert-butyl-4-methylphenoxy)aluminum alcoxide-based catalyst was investigated. The former shows much higher catalytic activity in chemical fixation of carbon dioxide than the latter. According to the experimental data, the unavoidable propylene carbonate resulting in an appreciable proportion in propylene oxide - carbon dioxide copolymerization reaction initiated by sterically hindered aluminum catalysts, seems to appear not at the back-biting reaction of the growing chain. Apparently the reaction temperature or the reaction components molar ratio did not influence the propylene carbonate proportion.

Keywords: propylene oxide, carbon dioxide, aluminium catalysts

Carbon dioxide is a non-expensive and non-toxic raw material for the chemical industry. On the other hand, the efficient transformation of carbon dioxide into useful chemicals is an important contribution to the environment protection, reducing the greenhouse effect. Among others, the copolymerization with epoxides and cycloaddition to epoxides are the most important chemical fixation processes of carbon dioxide. A widely used and investigated epoxide in these reactions is the propylene oxide (PO). Copolymerization results in polyether-polycarbonates [1-24] (considering only the first and the latest references) that can be useful components of polyurethane foams, or low cost CO_2-philes, that is they exhibiting miscibility with CO_2 under mild condition (temperatures under 100°C and pressures below 200 bar). By cycloaddition a high boiling point (240°C) valuable organic solvent, the propane-1,2-diol carbonate, called also propylene carbonate (PC), is obtained [25-35].

The catalysts used for copolymerization are complexes of organic compounds of zinc, such as diethyl zinc [1-4], dicarboxylic acids zinc salts [5-8,17], zinc phenoxides [10,13], aluminum derivatives like aluminum porphyrin systems [9,11,12], aluminum alcoxides stabilized with sterically hindered phenoxides [14-16], cadmium phenoxide [13], double metal cyanide complex based on $Zn_3[Co(CN)_6]_2$ [20], tetraphenylporphyrin [21] (salen)Cr catalysts [18,19,22] and (salen)Co(III)catalysts [23,24].

Among the highly active catalysts for carbon dioxide cycloaddition are those based on complexed aluminum prophyrinate [25,26], magnesium-aluminum mixed oxides [27], different metal oxide supported KI [28], magnesium oxide [29], Mg-Ni-containing smectite catalysts [30], polyfluoroalkyl phosphonium iodides [31], Zn based catalyst [32], quaternary ammonium salts [33]. In ref. [34,35] ionic liquids are used as catalyst. The propylene carbonate yield is about 10-15 % lower than the propylene oxide conversion, without specifying the by-product nature, and which, probably, is polypropylenecarbonate. The reaction mechanism is not very well known.

According to ref. [25] the insertion of PO between the aluminum (III) and chlorine might proceed *via* four-centered intermediates in CO_2 cycloaddition catalyzed by tetra-*t*-buthylphtalocyaninatoaluminum(III) chloride, and the carbon dioxide is reversibly inserted between the aluminum (III) and the axial ligand (chlorine or inserted propylene oxide).

If the cycloaddition catalyst is a mixed aluminum and magnesium oxide [28] is assumed that the addition reaction is initiated by adsorption of CO_2 on the Lewis basic sites, i. e. magnesium, giving a carbonate species, and independently, an epoxide is coordinated on the neighbouring acid site. The coordinated epoxide is ring opened by the nucleophilic attack of the carbonate species, which leads to an oxy anion species yielding the corresponding cyclic carbonate as a product.

When metal oxide (ZnO, ZrO_2, γ-Al_2O_3 or SiO_2) supported KI is used as catalyst, cycloaddition might take place [29] *via* the nucleophilic attack of the anion (I^- or O^-) on the least-hindered carbon of the epoxide, then CO_2 addition and the intramolecular cyclization, resulting in the formation of five-membered cyclic propylene carbonate.

Unlike cyclohexane oxide, which gives practically only copolymer and any by-product using the same catalysts, in PO-CO_2 copolymerization reaction an important quantity of PC results as by product, which is undesirable, but unavoidable. The cited polymer chemists consider that the PC results by the back-biting reaction of growing chain on the active sites.

In order to avoid, if possible, the PC appearance in PO copolymerization is necessary to make clear the reaction mechanism, and also the kinetics and thermodynamic.

The aim of this paper is to contribute to the better understanding of propylene carbonate formation reason during PO - CO2 copolymerization with sterically hindered aluminum phenoxide derivatives, and to develop new highly efficient catalyst for both, homo- and copolymerization of propylene oxide.

Experimental part

Materials

Triisobutylaluminum (TIBA) 1.0 M solution in toluene; 2,6-di-*tert*-butyl-4-methylphenol, 99 %; 2-propanol, 99.5 %, anhydrous (water < 0.003 %); %); methylphosphonic acid,

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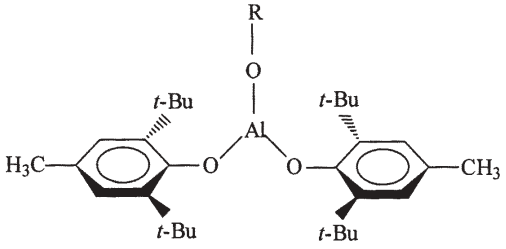
98 % (MPA); 2-methyl-2-propanol (*tert*-butanol), 99.5 %, anhydrous; toluene, 99.8 %, anhydrous (water < 0.002 %) tetrahydrofuran (THF), 99.9 %, anhydrous and inhibitor free (water < 0.003 %); 2-methoxyethyl ether (Diglyme) and 1,4-diazabicyclo[2,2,2]octane (DABCO) all substances were supplied by Aldrich and were used as received. Propylene oxide, 99 % (Aldrich) was used after distillation over calcium hydride under argon blanket. Carbon dioxide 99 % (Praxair and Penn Oxygen), research-grade (oxygen < 2 ppm, water < 3 ppm, CO < 0.5 ppm) was used as received. When needed, the reagents were handled under ultrahigh purity argon atmosphere (oxygen < 1 ppm, water < 3 ppm), supplied by Praxair.

Synthesis of the catalysts. The catalysts have been synthesized under argon blanket, in three-neck round bottom glass flasks, equipped with magnetic stirring bar and thermometer. Previously the flasks were heated to 150°C and then evacuated and flushed with the inert gas three times.

The syntheses of bis(2,6-di-*tert*-butyl-4-methylphenoxy) aluminum alcoxides, **1a** and **1b**, were performed typically using 20 mmoles (4.4072 g) of 2,6-di-*tert*-butyl-4-methylphenol and 10 mL of dry toluene. Stirring at room temperature (21°C) after 10 min a clear solution was obtained into which, using a glass syringe, previously heated and purged with argon, the triisobutylaluminum toluene solution (containing 10 mmoles TIBA) was added drop-wise. After the entire quantity of TIBA solution was introduced, the reaction vessel content was warmed to 40-50°C and maintained at this temperature for 4 h. Into the reaction mixture cooled to room temperature 10 mmoles of alcohol, (2-propanol or 2-methyl-2-propanol, respectively) were added drop-wise, with a syringe, previously purged with argon. The reaction mixture was warmed up again to 40-50°C and maintained at this temperature for 2 h. After reaction completion the catalyst results as 0.5 M concentration toluene solution, which was stored and handled under argon blanket at room temperature.

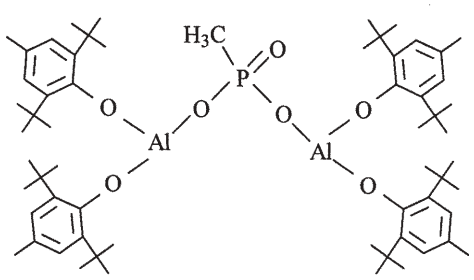
By analogy with the structure of bis(2,6-di-*tert*-butyl-phenoxy)methylaluminum [36], for **1a** and **1b** we propose the structure:



1a R = CH_3CHCH_3; **1b** R = $(CH_3)_3C$

The first step of the bis(2,6-di- *tert*-butyl-4-methyl-phenoxy)aluminum methylphosphonate, **2**, synthesis is the same as above described for **1a** and **1b**. The bis(2,6-di *tert*-butyl-4-methylphenoxy)isobutylaluminum has been cooled to 5°C, and the stoichiometric amount of methylphosphonic acid (5 mmoles, 0.48 g) was added dropwise as THF (5 mL) solution prepared in a dropping funnel. The above mentioned temperature was kept for 1 h. The catalyst **2** was used as 0.4 M concentration solution (with respect to the aluminum) in mixed solvents (toluene and THF), therefore is reasonable to assume, that Lewis acid **2** is complexed with the electron-donor THF.

For this compound we assume the following bidentate structure:



(2)

Relatively similar alkylaluminumphosphonate catalysts for propylene oxide homopolymerization have been reported in ref. [37].

Homopolymerization of propylene oxide. The catalysts synthesized as described above have been tested in propylene oxide homopolymerization, in order to get some information concerning their efficiency. These reactions have been carried out in toluene solution, under argon blanket in glass flasks equipped with magnetic stirring bar, thermometer and condenser purified as described above for catalyst synthesis. In these reactions 0.0715 moles of propylene oxide and 10 mL of toluene were used. The initial concentration of propylene oxide was about 4.3 mole.L^{-1} in function of the catalyst solution volume introduced into the reactor. The process was terminated with methanolic hydrochloric acid, the polymer solution was filtered using a 0.45 mm pore size Schleicher & Schuell membrane filter, and the toluene was removed under vacuum.

Copolymerization of propylene oxide with carbon dioxide. Copolymerization of propylene oxide with carbon dioxide was performed in 25 mL or 35 mL high pressure reactors, equipped with magnetic stirrer and pressure and temperature indicators. In order to cool or heat the reaction mixture, the reactor has been placed into a copper coil connected to a thermostat. The experimental setup is described in detail in ref. [38]. Prior to the experiment the reactor is heated to approx. 150°C, evacuated and cooled to room temperature under argon blanket. The propylene oxide was loaded first into the reactor using a syringe, and in the experiments using **2**, in order to diminish the initiation and propagation reaction rates as much as possible, PO was cooled to 10°C. The catalyst solution was injected also with a syringe. After reagents mixing and temperature stabilization, generally 1-2 min, the carbon dioxide was introduced into the reactor. The initial pressure of CO_2 and its density was chosen in function of the initial temperature in order to assure the desired carbon dioxide amount. Once loaded, the reactor was isolated and heated to the prescribed temperature. After the desired reaction time the reactor was cooled to the room temperature, the pressure was slowly released, and the reactor content was entirely transferred into a previously weighed 50 mL round bottom flask with chloroform. The unreacted propylene oxide, the solvents originated from the catalyst and chloroform were removed at 70°C under reduced pressure, obtaining a mixture of catalyst, copolymer and propylene carbonate, named **crude**. After weighing the crude, the propylene carbonate has been removed at reduced pressure (13 mbar) at 130°C, until disappearance of the corresponding IR spectrum peak at 1810 cm^{-1}. Weighing again the remaining product, the content of propylene carbonate results, as the difference between the mass of crude and copolymer + catalyst. After that the non-deactivated copolymer was dissolved in chloroform, terminated with methanolic hydrochloric acid, and the product was processed as described earlier.

Analyses. The IR spectra of the reaction products of polymerization were recorded with Genesis II FTIR

Table 1
HOMOPOLYMERIZATION OF PROPYLENE OXIDE IN TOLUENE

#	Catalyst	[PO]/[Al] molar ratio	Temperature in °C	Reaction time, in h	Yield in %
1	**1a**	40/1	45	24	34.2
2	**1a**	70/1	45	24	21.8
3	**1a***	70/1	45	24	26.8
4	**1a****	70/1	45	24	42.08
5	**1a**	35/1	85	24	97.2
6	**1a**	90/1	85	24	21.7
7	**1b**	40/1	45	24	32.6
8	**1b**	70/1	45	24	19.6
9	**2**	35/1	45	24	99.7
10	**2**	35/1	45	8	85.7
11	**2**	45/1	20	0.5	32.5

* Catalyst complexed with 2-methoxyethylether [Ether]/[I] = 1/1, molar ratio.
** Catalyst complexed with 2-methoxyethylheter [Ether]/[I] = 2/1, molar ratio.

spectrophotometer, on KBr windows. Representative peaks are at 1745 cm^{-1} and 1810 cm^{-1} wave-numbers corresponding to the carbonyl group from linear poly(propylene carbonate) and propylene carbonate (propane-1,2-diol carbonate), respectively. The latter is recorded at 1790 cm^{-1} in the case of pure propylene carbonate

The ^1H NMR spectra of copolymer solutions in $CDCl_3$ were recorded with a Bruker MSL 300 MHz spectrophotometer. The chemical shifts were considered against tetramethylsilane as internal standard. The carbonate linkage content of copolymer was calculated from the integrals of the peaks at ~ 3.6 ppm and ~ 4.6 ppm, corresponding to the methylenic protons from ether linkage and carbonate linkage, respectively.

Molecular mass distributions and molecular masses of the polymers were determined using a Waters 150 CV gel permeation chromatograph, equipped with 10^4, 10^3, 500 and 100Å Ultrastyragel columns, calibrated using monodispers polystyrene standards. The polymer sample solutions were prepared in THF (injection volume 400 mL) used also as eluent (flow rate 1 $mL.min^{-1}$). The GPC curves recorded, using the refractive index detector, were processed by the usual methods, computing the number average molecular mass, M_n, the weight average molecular mass, M_w and the first order polydispersity index, $i_1 = M_w/M_n$.

Results and discussions

Homopolymerization of propylene oxide

The PO homopolymerization reactions in toluene solution were carried out in order to test the catalyst efficiency. Table 1 summarizes the reaction conditions and resulted polymer yield. Using the **1a** and **1b** alcoxide terminated catalysts, the polymerization rate is rather slow at reasonable temperature (45°C), even at relatively high catalyst concentration, i.e. low [PO]/[Al] ratios. In the 35 mL steel reactor **1a** at higher polymerization temperature, 85°C, has been tested, but high polymerization rate, i.e. high polymer yield in a reasonable polymerization time, only at low [PO]/[Al] ratio was obtained.

Propylene oxide itself is a Lewis basis, able to form donor - acceptor complex with the aluminum of catalyst, a Lewis acid. Between complexed and non-complexed species equilibrium is established, which is determined by the donor - acceptor type bond strength. It is reasonable to assume that if this bond is strong enough, the active sites are blocked by the monomer. In order to diminish the PO access to the aluminum as complexing agent, the catalyst **1a** was complexed with 1,2-methoxyethylether prior monomer injection (table 1, entries 3 and 4). Polymerization rate increases with ether/catalyst molar ratio, but still remains at moderate values.

Because in carbon dioxide medium the polymerization occurs slower than in toluene solution, we focused on developing of a more efficient catalyst compared with **1a** or **1b**. According to the data presented in table 1, entries 9-11, catalyst **2b** allows very high reaction rates even at room temperature. The molecular masses of these polymers agreed well with the kinetic molecular mass, M_k, defined as

$$M_k = 58([PO]/[Al])X_{PO}$$

where 58 is the PO molecular mass, [PO] and [Al] are the molar concentration of propylene oxide and aluminum, respectively, and X_{PO} is the monomer conversion.

Also, the molecular mass distribution was narrow, with i_1 close to 1.1. Consequently it resulted that by this using this catalyst the PO homopolymerization is a controlled one.

Propylene oxide copolymerization with carbon dioxide

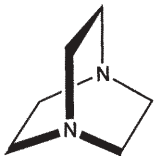
The experimental conditions and the results obtained with catalysts **1a** and **1b** in propylene oxide – carbon dioxide copolymerization reactions are shown in table 2.

As mentioned in the footnote of the table, entry 1 summarizes the mean values of five repeated trials using **1a**, carried out in order to test the reproducibility of the experiments and the proposed analytical methods. The used experimental methods for synthesis and analyses were proved to be reliable. The propylene oxide conversion was 42.83 wt.-%, the copolymer and propylene carbonate yield with respect to the loaded PO were 11.59 wt.-% and

#	Catalyst	CO_2 pressure at 21°C†, bar	$[CO_2]/[PO]$ molar ratio	Polym. temp., °C	Polym. time., h	Crude g/ g Al	Crude Copolymer content %	Carbonate linkage content of copolymer, mole %
1*	**1a**	69	6.1	60	24	36.06	18.18	9.10
2	**1a**	69	3.6	60	24	39.27	23.77	8.79
3	**1a****	70	6.2	60	24	21.13	21.51	8.21
4	**1a*****	70	5.5	60	24	0	0	0
5	**1a**	70	3.6	80	20	63.28	19.25	7.55
6	**1a**	55	0.8	80	20	45.30	30.40	8.69
7	**1a**	49	0.6	80	20	49.56	27.41	7.65
8	**1b**	69	3.6	60	24	37.93	29.16	8.35
9	**1b**	68	5.4	60	24	30.28	19.82	7.93

Table 2
POLYPROPILENE OXIDE CARBON DIOXIDE COPOLYMERIZATION, WITH CATALYSTS **1a** AND **1b**.[PO] / [I] = 25, MOLAR RATIO

† The initiation temperature;
* Mean results of 5 repeated trials.
**1a complexed with 2-methoxyethylether; [Ether]/[I] = 2/1
***1a complexed with 1,4-Diazabicyclo[2,2,2]octane (DABCO); [DABCO]/[I] = 1/1



#	[PO]/[I], molar ratio	CO_2 pressure at 21°C†, bar	$[CO_2]/[PO]$ molar ratio	Polym. temp., °C	Polym. time., h	Crude g/ g Al	Crude Copolymer content %	Carbonate linkage content of copolymer, mole %
1	35	78	4.3	40	48	73.04	45.68	5.27
2	35	68	7.2	40	48	74.07	50.57	6.94
3	50	81	4.7	40	48	79.90	48.12	6.63
4	50	68	7.4	40	48	79.85	50.86	5.94
5	75	70	7.9	40	48	38.08	53.10	6.21
6	50	81	4.7	60	20	87.52	45.42	5.65
7	50	70	7.5	60	20	90.31	45.94	6.12
8	75	82	5.0	60	20	72.47	43.97	6.67
9	100	82	5.1	60	20	171.13	47.14	6.89
10	35	64	6.8	80	20	50.07	51.08	5.85
11	50	79	4.5	80	20	60.98	52.59	5.78
12	50	68	7.2	80	20	87.79	55.07	6.55
13	75	70	7.7	80	20	101.36	63.35	6.67
14	100	70	7.8	80	20	78.79	41.79	5.98

Table 3
PROPYLENE OXIDE - CARBON DIOXIDE COPOLYMERIZATION INTIATED BY **2**

† The initiation temperature

31.24 wt.-%, respectively. The obtained copolymers carbonate linkage content was about 8-9 mole-%. Also, in the case of these trials the molecular mass distribution of non-deactivated copolymer and of those after propylene carbonate removal and deactivation, were M_n = 24,175 g/mole and i_1 = 1.05 for crude copolymer and M_n = 23,575 g/mole and i_1 = 1.06 for the final copolymer, respectively. Surprisingly, the heterogeneity index has extremely low values, the copolymer being practically a monodisperse one, which is not characteristic for this type of

copolymerization. The propylene carbonate is distilled off from copolymer under sever conditions: at 130°C over 6-8 h. The kinetic molecular mass, considering the [PO]/[I] molar ratio, the carbonate linkage content and copolymer yield, is less than 200 $g.mole^{-1}$. To get the experimental molecular mass the [PO]/[I] must be over 400 even at 100 % yield, or about 4000 for the mentioned yield.

These data show that the propylene carbonate in PO - CO_2 copolymerization with sterically hindered aluminum based catalysts is not given by back-biting reaction. If back-biting occurs, the molecular mass of the resulting copolymer must be considerably lower than the kinetic molecular mass and, also, the molecular mass distribution of such a polymer should be broader.

Besides, by heating for 8-10 h the copolymer, which contains the active catalyst, the molecular mass remains practically the same. In case of back-biting the molecular mass should decrease because of this thermal treatment.

Another interesting conclusion is that the main part of the catalyst is actually a propylene carbonate producing catalyst, and only a very small fraction of the sterically hindered aluminum alcoxide allows really a controlled copolymerization.

It seems that apparently the sterically hindered aluminum alcoxide provides two kinds of active sites: the active sites initiating the copolymerization which will be involved only in this reaction and those which started to produce propylene carbonate and will make it until the reaction is stooped. Is not clear at all what is the reason for appearance of these sites, but it is possible that the monomer access and complexation to the aluminum is responsible for these two type of active centers.

With qualitative purposes, several trials (trials are not in the tables) were carried out in a 55 mL steel high pressure view-reactor equipped with sapphire windows and heating rods, in order to observe the phase behavior during polymerization at [PO]/[I] =25 molar ratio. The carbon dioxide pressure at the initiation temperature, 21°C, was 83 bar, that is $[CO_2]/[PO] = 11.3$, increasing up to 280 bar at 60°C, the reaction temperature. The reaction temperature has been reached 1 h after carbon dioxide loading. The reaction mixture was fully transparent for 1.5 h that is the reaction mixture was homogeneous, and is reasonable to assume that at least the initiation step is homogeneous reaction. Later the reactor content became more and more cloudy, possibly because the catalyst bonded to copolymer is less soluble in the reaction medium in these conditions. These trials were stopped after 4 h. It is interesting to remark that , the copolymer yield was very low, not enough for quantitative analysis, but the propylene carbonate presence has been proved by the appearance of the peak at 1810 cm^{-1} in IR spectrum. This means that both, copolymer and propylene carbonate are obtained in parallel reactions and not by back-biting one.

Based on this assumption we tried to limit the PO access to the aluminum of catalyst by complexation with Lewis bases that have more than one electron donor atom in their molecule. The complexation reaction was carried out prior to PO and carbon dioxide admission. Using 2-methoxy-ethylether at the molar ratio that was the most effective in homopolymerization, no improvement was observed (table 2 by entry 3), even the turnover was the smaller. By complexation with DABCO both, the propylene carbonate and copolymer have been inhibited (table 2 by entry 4).

The [CO2]/[PO] ratio or reaction temperature practically had no significant effect on copolymer or propylene carbonate proportion in crude. The latter improved, as expected, the crude yield.

Substituting the 2-propoxy radical in the catalyst molecule with the bulkier *tert*-butoxy one (table 2, entries 8 and 9) the results were very similar with those obtained with the former.

Also, it is interesting to remark that in all copolymer, irrespectively to the reaction conditions, the carbonate linkage content was the same, about 8-9 %.

Considering that the active site nature, i.e. copolymerization one or propylene carbonate producing one, is determined *ab initio* by the two competitive reactions, and the faster the initiation the higher the copolymer yield, the more active methylphosphonic acid derivative has been tested in PO – carbon dioxide copolymerization reaction. The experimental conditions and results are shown in table 3 the trials being grouped with respect to the temperature.

Unlike the much less active catalysts **1a** and **1b**, here experiments were carried out even at 40°C reaction temperature. Because the reaction rate is considerably slower in liquid carbon dioxide than in toluene, the reaction time was extended to 48 h and rather high crude yields have been obtained.

The experimental conditions and the results obtained with catalyst **2** in reaction of propylene oxide with carbon dioxide are given in table 3.

As usual, we give in both, tables 2 and 3, the so-called turnover expressed in gram product per gram aluminum, in order to describe the reaction yield. In fact this is not a quite good parameter for the most polymerization reactions – except those really catalytic ones, like the Ziegler-Natta type super-active polymerizations – because the lower the catalyst concentration the higher the turnover. On the other hand the catalyst concentration or the monomer to catalyst ratio is determined by the desired molecular mass of the polymer. Therefore the turnover does not reflect exactly the yield or conversion.

Obviously, using catalyst **2**, the crude yield is much higher than in copolymerization reactions initiated by **1a** and **1b**. The number average molecular mass of the synthesized copolymers is situated between 18,000 and 24,000, lower than in previously catalysts described in table 2, but much higher as expected based on [PO]/[I] ratios. The heterogeneity index was 1.1-1.3, that is these copolymers have a little broader molecular mass distribution than those synthesized with **1a** and **1b**, but still rather narrow. In these we observed cases some increase of molecular mass with the monomer to catalyst ratio as well. From this point of view these reactions are a little closer to the usual known systems.

The carbonate linkage content of the copolymers is a little lower as obtained with catalysts **1a** and **1b**: between 5 and 7 mole-%.

Also, the propylene carbonate proportion is significantly reduced, but still high. The [PO]/[I] and [CO2]/[PO] ratio or the reaction temperature seems to have no influence on it.

Conclusions

The unavoidable propylene carbonate resulting in an appreciable proportion in propylene oxide - carbon dioxide copolymerization reaction initiated by sterically hindered aluminum alcoxides does not appear by the back-biting reaction of the growing chain. Is not clear yet the reaction mechanism responsive for the appearance of this compound.

Apparently the reaction temperature or the reaction components molar ratio does not influence the propylene carbonate proportion.

A new sterically hindered bis(phenoxy)aluminum methylphosphonate catalyst has been synthesized which is very active in propylene oxide homopolymerization allowing to increase the copolymer yield and to diminish the propylene carbonate proportion in the reaction product.

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