Kinetics of Ring-Opening Polymerization of α-angelicalactone Initiated by Sodium and Aluminum Alcoxides

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Abstract. Biodegradable and biocompatible polyesters, obtained from renewable plant materials, are of great interest due to their use in various industries. The kinetics of anionic ring-opening polymerization (ROP) of α-angelicalactone (αAL) initiated by sodium alcoxides and aluminum isopropoxide has been studied. The kinetics of the process is described by the first order equation in terms of αAL concentration. An increase of the initiator concentration increases the first order rate constant and the αAL conversion, but reduces the molecular weight of the resulting polymers. The maximum αAL conversions (≥0.99) and molecular weights of polymers (26000–29000) were obtained in non-polar solvents, toluene and carbon tetrachloride, and in the bulk at 373–403 K for 60–250 hours.

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Кинетика полимеризации α-ангеликалактона с раскрытием кольца, инициированной алкоголятами натрия и алюминия

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Аннотация. Биоразлагаемые и биосовместимые полиэфиры, получаемые из возобновляемого растительного сырья, вызывают большой интерес к их применению в различных отраслях. Изучена кинетика анионной полимеризации (ROP) α-ангеликалактона (αАЛ), инициированной алкоголятами натрия и изопропилатом алюминия. Кинетика процесса подчиняется уравнению первого порядка по концентрации АЛ. Рост концентрации инициатора увеличивает константу скорости первого порядка и конверсию αАЛ, но снижает молекулярную массу получаемых полимеров. Максимальные конверсии αАЛ (≥0,99) и молекулярные массы полимеров (26000–29000) получены в неполярных растворителях, толуоле и четыреххлористом углероде, и в массе без растворителя при 373–403 K в течение 60–250 ч.

Ключевые слова: α-ангеликалактон, полимеризация с раскрытием цикла, алкоголяты натрия и алюминия.

Introduction

Ring-opening polymerization of cyclic esters (lactones, lactides, or cyclic carbonates) is a widely used method for the synthesis of polyesters with controlled molar mass, narrow polydispersity, and desired macromolecular structures. [1–3]. Homo- and copolyesters are very perspective for biomedical applications and industrial materials as alternatives to usual polyolefins [4–6].

Among the wide variety of investigated cyclic esters, a five-membered 5-methylfuran-2(3H)-one, often called α-angelicalactone (αAL, Fig. 1) can be obtained from renewable plant materials.

Generally saturated five-membered lactones do not polymerize with ring opening [7], but a double bond in the ring can activate this polymerization route. For example, the change in Gibbs free energy for ring-opening polymerization of γ-butyrolactone is positive (ΔG^0(ROP) = 13 kJ/mol) [8]. Unlike
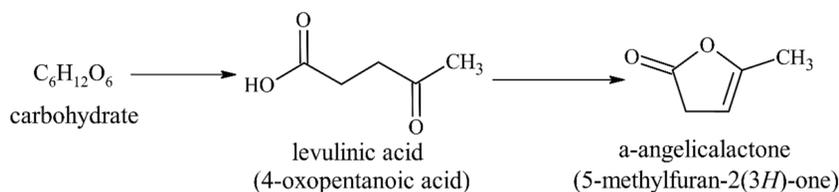
Fig. 1. Scheme of αAL obtaining

poly[oxidiyl(4-methyl-1-oxobut-3-en-1,4-diyl)]
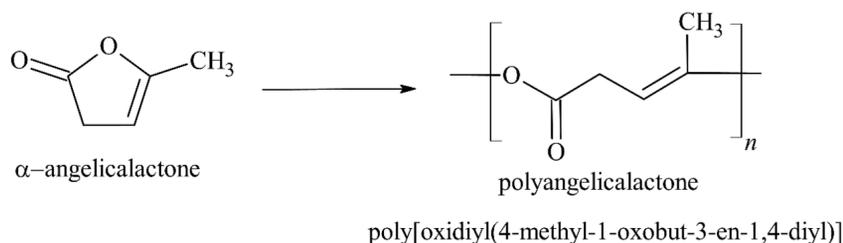
Fig. 2. Scheme of αAL ring-opening polymerization

γ-butyrolactone, αAL ring contain a double bond and this probably activates αAL for ring-opening polymerization (ΔG^0(ROP) = –20.7 kJ/mol, Fig. 2) [9]. According to these data, the equilibrium constant can reach values of 300–500, and the αAL conversion during polymerization can exceed 99–99.5 %.

In 2006, we reported the polymerization of αAL using sodium butoxide. Bulk polymerization at 291 K and the presence of 3–5 mol.% sodium butoxide did not achieve complete conversion even after a long reaction time (82 % in 250 h), the resulting oligomers had a low molecular weight (M_w = 1120–1800 g/mol) with moderate polydispersity (K_D = 1.8) [10]. αAL homopolymers with molecular weights up to 19500 g/mol were obtained at the presence of sodium isopropoxide [11]. Later, a similar polymerization process catalyzed by tin octanoate was reported. The polymerization conversion in toluene at 403 K and [αAL]$_0$/[Sn]$_0$ = 300 was 80–85 % at 30–50 hours and resulting polymers had a molecular weight M_w = 29357 g/mol with a polydispersity K_D = 1.25 [12].

The low αAL conversions in known experimental studies do not reach the maximum values predicted by the thermodynamics of the process, and this complicates the isolation and purification of the resulting polyangelicalactone. The goal of this work is to study the kinetics of αAL ring-opening polymerization initiated by sodium and aluminum alcoxides and to achieve the maximal monomer conversion of the process.

Materials and methods

α-Angelicalactone, purchased from Alfa Aesar (98 %), was purified by fractional crystallization from the melt. The total content of impurities was estimated using ^{1}H-NMR spectroscopy and was 0.10±0.02 mol.%. Impurities were not identified. During storage (9 months or more) and during the study, the samples did not show a noticeable tendency to spontaneous polymerization. Sodium butoxide (ButONa), sodium propoxide (PrONa), and sodium isopropoxide (i-PrONa), as well as aluminum triisopropoxide ((i-PrO)$_3$Al) were used as αAL polymerization initiators. Sodium butoxide was synthesized as described in [13]. Sodium propoxide and isopropoxide were prepared by reacting

sodium metal with propyl and isopropyl alcohol, respectively. Aluminum triisopropoxide was prepared according to the procedure [14]. Toluene and tetrahydrofuran were dried at reflux over a benzophenone-Na complex and distilled under argon. Carbon tetrachloride, chloroform, and dichloromethane were dried at reflux over phosphorus pentoxide and distilled under argon.

αAL bulk polymerization: 0.98 g (0.01 mol) of αAL was placed in a glass tube, the calculated amount of initiator was added, the tube was purged with argon, sealed, and placed in a thermostat. After a predetermined time, a sample of 10 microliters was taken off from the reaction mass. The sample was mixed with 1 ml of 1 % HCl solution in ethanol and analyzed by GLC (Chromos Engineering GH1000 chromatograph, column 30 m B 0.32 mm, stationary phase 25 % trifluoropropylsiloxane, column temperature 180^0 C, anthracene was used as internal standard).

αAL polymerization in solution: 10 ml of a 1M solution of α-angelicalactone in the appropriate solvent was placed in a glass tube, the calculated amount of initiator was added, the tube was purged with argon, sealed, and placed in a thermostat. After a predetermined time, a sample of 10 microliters was taken off from the reaction mass, mixed with 1 ml of 1 % HCl solution in ethanol and analyzed by GLC.

The αAL conversion degree (α) was determined by GLC. The conversion value was calculated using the following equations:

  – for bulk polymerization: $\alpha = m_t(\alpha\mathrm{AL})/m_0(\alpha\mathrm{AL})$
  – for solution polymerization: $\alpha = [\alpha\mathrm{AL}]_t/[\alpha\mathrm{AL}]_0$

The apparent rate constants (k_a) were determined from the slope of the initial linear segments of the dependence $\ln([\alpha\mathrm{AL}]_0/[\alpha\mathrm{AL}]_t)$ versus time at αAL conversion less than 5 %.

Weight average molecular weights (M_w) were determined viscometrically at 298 K in chloroform, from the equation: $[\eta] = 5{,}15 \times 10^{-4} \times M_w^{0.7}$.

Number average molecular weights (M_n) were determined by GPC. The samples were dissolved in the mobile phase (~5 mg/ml) and filtered through a 0.22 μm PTFE membrane filter. A Waters 2690 XE Separations Module with light scattering detection and an Agilent 1260 Infinity II Multi-Detector GPC/SEC System with triple detection: refractometric, viscometric and light scattering was used. Mobile phase for Waters 2690 XE was mixture of acetonitrile and tetrahydrofuran (acetonitrile/THF = 58/42), eluent flow 1.2 ml/min. The mobile phase for the Agilent 1260 Infinity II was THF, the eluent flow is 1 ml/min. The devices were calibrated by polydisperse samples of polystyrene.

The polydispersity index (K_D) was calculated according to the equation: $K_D = M_w/M_n$

Results and discussion

The dependences of the polymerization efficiency of αAL on time (Fig. 3) and initiator concentration (Table 1), the solvent nature (Table 2) and temperature (Tables 3, 4) were studied.

The dependences of the αAL conversion on time in the coordinates of the first-order kinetic equation are linear (Fig. 3), i.e. polymerization is adequately described by a first order reaction with respect to the αAL concentration.

The obtained values of the polymerization rate constant increase with increasing the initiator concentration, but non-linearly, including in logarithmic coordinates (Fig. 4). The tangent of the slope in these coordinates is equal to the reaction order with respect to the reactant concentration, and it shows a decrease of the order from about 2 to ½.
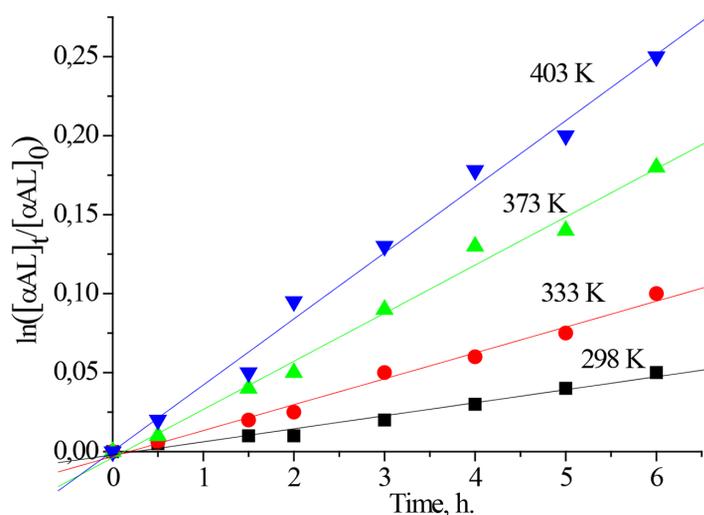
Fig. 3. Dependences of the αAL conversion on time in the coordinates of the first-order kinetic equation at 298–403 K. 1M αAL in toluene, initiator (I) – (i-PrO)$_3$Al, $[αAL]_0/[I]_0 = 200$

Table 1. Influence of the nature and initiator concentration on the αAL conversion, the molecular weight of polyesters obtained by bulk polymerization for 250 hours, and the polymerization rate constant at 298 K.

Initiator (I)	$[αAL]_0/[I]_0$	α	M_w	M_n	K_D	$k_a \times 10^7$, sec.$^{-1}$
ButONa	20	0,838	2368	1280	1,85	13,1
	35	0,658	2564	1535	1,67	9,89
	100	0,32	5964	4113	1,45	4,33
	200	0,097	10620	8296	1,28	1,35
PrONa	20	0,859	2144	1146	1,87	14,1
	35	0,67	2661	1583	1,68	11,3
	100	0,315	6680	4282	1,56	5,28
	200	0,081	12460	11125	1,12	1,77
i-PrONa	20	0,721	2890	1489	1,94	14,5
	35	0,542	3791	2369	1,6	11,2
	100	0,257	8993	5728	1,57	5,24
	200	0,069	16707	14527	1,15	1,58
(i-PrO)$_3$Al	20	0,881	2942	1564	1,88	14
	35	0,707	3303	1866	1,77	10,7
	100	0,382	8337	5830	1,43	4,81
	200	0,166	15678	13998	1,12	1,29

Table 2. Influence of the solvent nature on the 1M αAL conversion and the molecular weight of polyesters obtained by polymerization in solution, $[αAL]_0/[I]_0 = 200$, for 60 hours, and the polymerization rate constant at 298 K.

Initiator (I)	Solvent	α	M_w	M_n	K_D	$k_a×10^7$, sec.$^{-1}$
ButONa	TGF	0,514	10350	6854	1,51	14,28
	toluene	0,841	17857	11671	1,53	23,36
	CCl$_4$	0,976	19634	12917	1,52	27,11
	CHCl$_3$	0,019	4830	3220	1,5	0,52
	CH$_2$Cl$_2$	0,009	2360	1595	1,48	0,25
PrONa	TGF	0,628	12692	8576	1,48	17,44
	toluene	0,906	18136	12594	1,44	25,17
	CCl$_4$	0,978	19631	13922	1,41	27,17
	CHCl$_3$	0,093	1869	1280	1,46	2,58
	CH$_2$Cl$_2$	0,067	1359	906	1,5	1,86
i-PrONa	TGF	0,717	14416	9182	1,57	19,92
	toluene	0,917	18402	12604	1,46	25,47
	CCl$_4$	0,987	19751	12909	1,53	27,42
	CHCl$_3$	0,137	2750	1883	1,46	3,81
	CH$_2$Cl$_2$	0,091	2400	1538	1,56	2,53
(i-PrO)$_3$Al	TGF	0,747	18230	12401	1,47	20,75
	toluene	0,975	24420	16841	1,45	27,08
	CCl$_4$	0,982	10820	6597	1,64	27,28
	CHCl$_3$	0,19	9680	6496	1,49	5,28
	CH$_2$Cl$_2$	0,128	8460	6130	1,38	3,56

Table 3. Influence of temperature on αAL conversion, polymerization rate constants, and molecular weight of bulk polymerized polyesters for 250 hours

Initiator (I)	T, K	α	M_w	M_n	K_D	$k_a×10^7$, sec.$^{-1}$
ButONa	298	0,097	10620	8296	1,28	1,35
	333	0,54	14879	11370	1,31	7,58
	373	0,84	16667	14522	1,15	39,58
	403	0,92	18234	16651	1,1	110,23
PrONa	298	0,081	12460	11125	1,12	1,77
	333	0,53	15606	13460	1,16	8,82
	373	0,64	17480	15851	1,1	41,43
	403	0,93	18886	17461	1,08	108,05
i-PrONa	298	0,069	16707	14527	1,15	1,58
	333	0,42	17284	16307	1,06	8,28
	373	0,69	19360	18123	1,07	40,65
	403	0,92	20917	19362	1,08	108,97
(i-PrO)$_3$Al	298	0,166	15678	13998	1,12	1,29
	333	0,93	21685	17783	1,22	7,39
	373	≥0,99	24290	21651	1,12	39,29
	403	≥0,99	26243	24887	1,05	110,62

Table 4. Influence of temperature on 1M αAL conversion, polymerization rate constants, and molecular weight of polyesters obtained by polymerization in toluene, $[αAL]_0/[I]_0 = 200$, for 60 hours.

| Initiator (I)	T, K	α	M_w	M_n	K_D	$k_a \times 10^6$, sec.$^{-1}$
ButONa	298	0,841	17857	11671	1,53	2,34
	333	0,894	19202	12801	1,5	4,84
	373	0,982	21605	16367	1,32	7,58
	403	≥0,99	23020	11685	1,97	10,02
PrONa	298	0,906	18136	12594	1,44	2,52
	333	0,952	19560	11306	1,73	4,47
	373	0,966	19733	10016	1,97	7,34
	403	≥0,99	20018	10480	1,91	10,04
i-PrONa	298	0,917	18402	12604	1,46	2,55
	333	0,943	19076	13273	1,39	4,91
	373	0,981	19866	13156	1,51	8,06
	403	≥0,99	20123	12899	1,56	10,71
(i-PrO)$_3$Al	298	0,975	24420	16841	1,45	2,71
	333	0,977	24836	20357	1,22	4,78
	373	≥0,99	25769	13491	1,91	8,19
	403	≥0,99	28795	20865	1,38	10,93
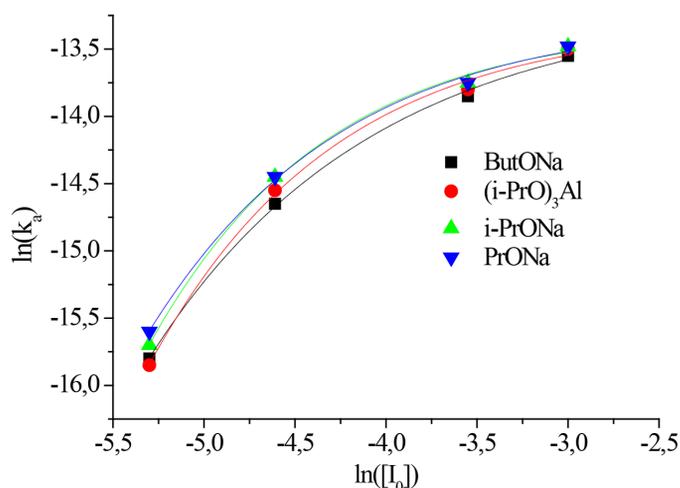
Fig. 4. Influence of initiator concentration on the observed first-order rate constant of the polymerization process. Conditions see Table. 1

The polymerization rate decreases in a series (Table 2):

$$CCl_4 > toluene > THF > CHCl_3 > CH_2Cl_2,$$

Table 5. Activation energy of the polymerization in bulk (1) and in toluene (2).

Initiator (I)	E_a, kJ/mol	
	(1)	(2)
ButONa	41,89	13,70
PrONa	39,13	13,11
i-PrONa	40,28	13,63
(i-PrO)$_3$Al	42,35	13,36

The highest rates were achieved in non-polar solvents, carbon tetrachloride and toluene. This is obvious, since solvents with a low dielectric permittivity increase the Coulomb attraction of the alkoxide anion and the αAL dipole and reduce the delocalization degree of the alkoxide ions.

The activation energy of polymerization (E_a) does not depend on the nature of the initiator (Table 5), its value for the process in bulk (40.9 ± 1.8 kJ/mol) is three times higher than the polymerization index in toluene (13.45 ± 0.34 kJ/mol). This ratio qualitatively corresponds to the effect of the dielectric constant of the medium on the kinetics of the process noted above.

The rate constants of polymerization in the bulk and in toluene at high temperature (403 K) practically coincide. At low temperature (298 K) the rate constant in the bulk is approximately 20 times lower compared to the process in toluene according to the difference of activation energies in the bulk and toluene.

The polymerization rate constants are practically independent of the initiator nature in the considered series of metal alcoxides. This corresponds to the well-known concept that the growth of the lactone polymerization chain occurs at its end, which is remote from the initiator [1].

The dependences of the αAL conversion on the process conditions correlate well with similar results of rate constants. In the best solvents (CCl$_4$ and toluene) and during bulk polymerization, the monomer conversion exceeds 90 % in many experiments. A conversion of 99 % is attained on all used catalysts in toluene at 373–403 K, and in bulk – on aluminum isopropoxide at 403 K.

The molecular weights of M_w and M_n increase from 2300 (M_w) –1300 (M_n) to 17000–14000 g/mol with a decrease in the initiator concentration in the range of selected conditions (Table 1). The influence of the initiator nature is insignificant: sodium and aluminum isopropoxide give one and half times higher molecular weights compared to sodium butoxide and propoxide (Table 2). An increase of polymer molecular weights by a factor of 5–10 is observed at passing from polar solvents to nonpolar ones and into the bulk, and this dependence correlates with the solvent effect on the process rate and αAL conversion. The molecular weights of polymers slightly (by 10–20 %) increase with increasing temperature in the range of 298–403 K (Table 3, 4).

Conclusion

The obtained results show that in order to obtain polymers of α-AL with high characteristics (monomer conversion over 99 %, weight average molecular weights over 25000 g/mol), it is recommended to carry out the process with minimal amounts of polymerization initiators based on isopropoxides ([αAL]$_0$/[I]$_0$ ≥ 200) in non-polar solvents or in bulk at high temperatures (373–403 K). The attained maximum conversions of αAL (more than 99 %) exceed all known literature data and

open up new possibilities for creating efficient technologies for the production of polyangelicalactone, a biodegradable polymer based on renewable plant materials.

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