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New Biodegradable Polymers Based on α -Angelicalactone

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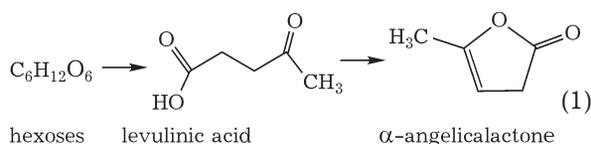
Abstract

A possibility was demonstrated for the polymerization of α -angelicalactone (5-methyl-2(3H)furanone) according to two main routes – by opening the olefin and/or opening lactone bond. Polyesters of α -angelicalactone were obtained using basic catalysts. Liquid and solid polymers with the molecular mass (MM) ranging from 840 to 100 000 were synthesized. Using ^1H NMR method it was demonstrated that the fraction of polyester intermonomer bonds therein amounts to 60–68 %. The copolymers of α -angelicalactone with styrene additives were obtained exhibiting MM of about 200 000–500 000. It was demonstrated that the polymers obtained yield to biodegradation by various microorganisms during a month to half-year period.

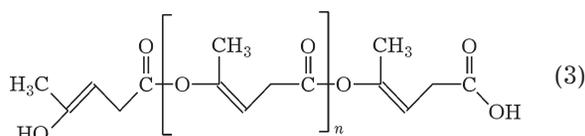
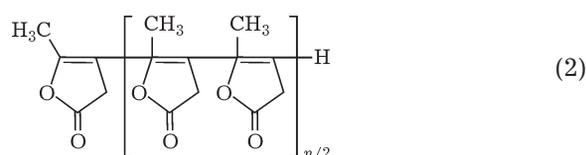
Key words: angelicalacton, biodegradable polymers, styrene, copolymers, polyesters, catalytic polymerization

INTRODUCTION

The α -angelicalactone (5-methyl-2(3H)-furanone, AL), the product of levulinic acid dehydration, can be obtained from hexose carbohydrates as a renewable natural raw material:



The structure of the AL molecule involves two functional groups capable of participating in the reactions of polymerization, such as the ester group and the double bond conjugated therewith. Correspondingly, there are two possible routes of polymerization opening the double bond with the formation of polyfuranone (2) and opening the lactone cycle with the formation of polyester (3):



In the case of polymerization through the double bond, the AL could be considered doubly-substituted vinyl acetate. Such compounds wherein substituents are located at the ends of the vinyl groups, are mainly not polymerized, but the presence of the lactone ring to a somewhat extent causes protons in positions 2 and 3 to be mobile [1]. This results in the possibility of double bond migration within the molecule under changing of physical conditions [2] as well as in opening the π -bond in the presence of Lewis's strong acids and under the action ionizing radiation [3]. As a result, oligomeric products are obtained with the polymerization level $n = 5-8$. Anionic dimerization according to route (2) occurs only with intensive mechanical activation [4]. The products of polymerization *via* route (3) are known, formed under the action of basic catalysts on AL [5]. The AL could be used as an olefin component in the reactions

of copolymerization with methyladamantyl methacrylate, maleic anhydride, norbornene [6], and polyhydroxystyrene [7]. In all the cases the fraction of AL in the copolymer does not exceed 30 %.

Of the greatest interest are the reactions of AL polymerization with opening the lactone cycle. The products of such reactions could exhibit the ability of biodegradation [8–10]. We have not found any literature data concerning the polymerization of such substituted γ -lactones, which was also mentioned by the authors of [11, 12]. The catalysts of AL polyester interchange reaction can be represented by inorganic and organic bases [13], organometallic compounds [14].

The purpose of the present work consists in the studies on AL polymerization and copolymerization as well as on the biological degradability of polymers obtained.

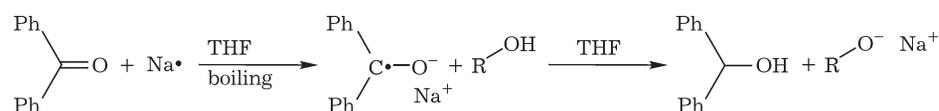
EXPERIMENTAL

Levulinic acid was purchased from Acros Organics (Morris Plains, NJ, USA) as well as that synthesized according to [15]. The α -angelicalactone was obtained from levulinic acid in the mode of vacuum distillation (25 Torr, 340–345 K) and then it was purified by fractional crystallization from melt. The total content of impurities was estimated with the help of ^1H NMR spectroscopy amounting to (0.10 ± 0.06) mol. %. The impurities were not identified. Under storage (9 months and more) and in the course of investigations, the samples did not demonstrate any considerable tendency to spontaneous polymerization.

Dioxane, ethyl acetate, diethyl ether, dichloroethane, butanol-1, propanol-1, propanol-2, benzophenone ("kh. ch." (chemical pure) grade) were additionally purified *via* fractional distillation under vacuum.

As oxide catalysts, we used benzoyl peroxide ("kh. ch." (chemical pure) grade) and acetone peroxide obtained according to [13].

As the basic catalysts we used NaOH ("ch.d.a." (analytical) grade), sodium butylate synthesized according to [16]. For the experiments in anhydrous media, alcoholates were synthesized according to the scheme



To a beaker flask 0.25 L in capacity with a backflow condenser was placed carefully drained tetrahydrofuran (THF), benzophenone, sodium metal (fine flakes) counting upon the concentration of ketyl formed equal to $((0.3-0.8) + 1.5X)$ M

where X stands for the required initial concentration of alcoholate. The excess ketyl is consumed for the elimination of residual water (up to 10^{-12} M of water) as well as dissolved oxygen and carbon oxides. After the formation of ketyl, into a flask under feeding a flow of argon were loaded corresponding components for the synthesis of the initiator *in situ* according to literature technique [17] counting upon the obtaining of a necessary concentration and then of α -angelicalactone.

As the acid catalyst we used boron trifluoride etherate ("ch." (pure) grade).

The purity of substances was estimated using GLC technique and ^1H NMR method. The NMR spectroscopy was also involved in the investigation of polymeric product structure. The NMR spectra of substances were registered using a Bruker DPX-200W spectrometer (200 MHz) at the Multi Access Centre of the Krasnoyarsk Scientific Centre of SB RAS with reference to the deuterium signal of solvent.

Molecular masses (MM) and polydispersion indices $n = M_w/M_n$ of the obtained products of polymerization were estimated viscosimetrically (Osvald viscosimeter, capillary diameter of 0.12 and 0.56 mm, benzophenone) and cryoscopically in benzophenone [18].

The biodegradation ability of polymers obtained was estimated according to an increase in the biomass of microbial cultures *Saccharomyces cerevisiae*, *Candida parapsilosis*, *Streptomyces chrysomallus*, *Streptomyces lividans* and according to visually observed polymer dissolution. To a weighed portion of the suspension of microbial culture (0.5 g, $\sim 10^7$ – 10^8 CFU) we added a weighed portion of the polymer (3 g) and 2 mL of an aqueous solution containing 1.45 M NaCl, 1.19 M $(\text{NH}_4)_3\text{PO}_4$, 0.48 M MgSO_4 . In order to estimate the biodegradation of polymer in a non-mineralized substrate we prepared

a similar sample from 0.5 g of microbiological culture suspension, 3 g of polymer and 2 mL of distilled water. The samples prepared were kept at (308 ± 1) K during 5–30 days. The completeness of polymer degradation was observed visually and the time of its complete dissolution was estimated from the disappearance of resin samples. The increase of microorganisms was estimated from the increase in dry mass of the weighed substances and optical density (absorbance) of the cultural liquid ($\lambda = 540$ nm, cell thickness 1 cm, nephelometric method), diluted up to a level required.

In order to estimate the ability of the polymers obtained with respect to biodegradation in soil, we performed model experiments with the samples of grey wood soil. The clod of soil was divided into nine-ten equal parts (by mass); each part was placed in a separate vessel. With the help of a tubular applicator we placed polymer samples with the mass from 6 to 8 % of the mass of soil (3–5 g on the average), into the bulk of soil samples. The temperature of vessels was taken to be equal to the temperature of air and amounted to 286–298 K for all the observation period. The humidity of soil was maintained by a periodic surface watering. In order to prevent the influence of rhisodegradation we performed a regular careful weeding of the samples of soil [19].

The statistical estimation of the toxicity of aqueous extracts from soil samples resulted from the degradation of PAL and PAL/styrene material was carried out using a multicell cultivator KVM-05 with the culture of daphnids according to standard regulations PND F T 14.1:2.3:4.10-04 16.1:2.3:3.7-04.

RESULTS AND DISCUSSION

Effect of peroxide initiators

The organic peroxides used (benzoyl and acetone peroxide) are inefficient as initiators of AL polymerization. Under exposure of the reaction mixture within the range of “operating” temperature (385–388 K for benzoyl peroxide and 393–400 K for acetone peroxide) for many hours [13] no considerable consumption of monomer in the mixture with initiators, according to ^1H NMR data, was observed.

Cationic polymerization of α -angelicalactone

As Lewis acid we used the complex of boron trifluoride with diethyl ether, for obtaining a compound with known structure [1]. In 25 mL of carbon disulphide, we dissolved 10 g AL, and then we added 0.25 mL of boron trifluoride etherate. The mixture obtained was kept during 5 h at the temperature of (323 ± 5) K. After the separating from the reaction mixture, washing with diethyl ether and vacuum distillation of volatile substances we obtained 8.8 g of highly viscous dark red coloured resin, soluble in acetone, dioxane and alcohols, low-soluble in an aqueous solution of NaOH, insoluble in water, diethyl ether, benzene and paraffins. Molecular mass $M_n = 810$, $M_w = 862$.

Figure 1 demonstrates ^1H NMR spectrum obtained for the products of interaction between α -angelicalactone with boron trifluoride in pyridine D6 in the presence of ethyl acetate. Identified signals are the following: pyridine (δ 8.6–8.7,

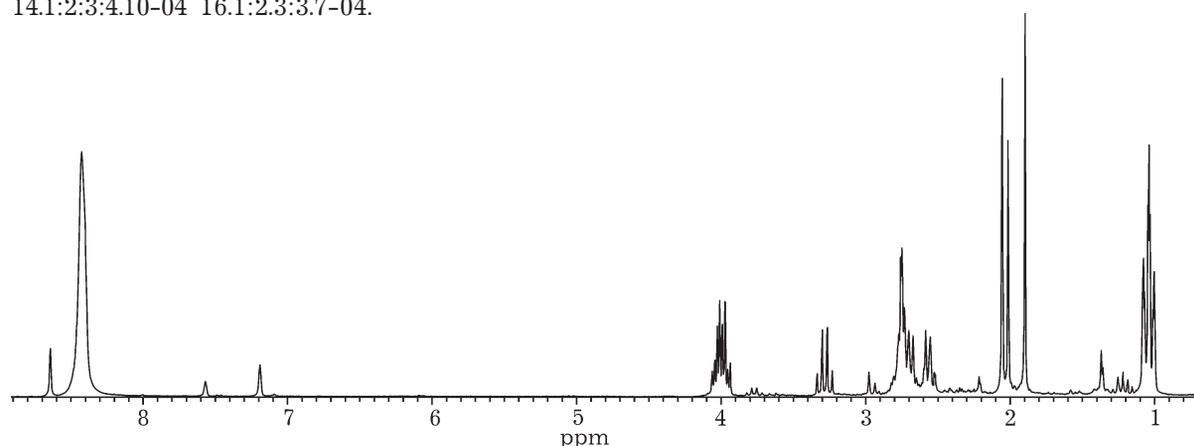


Fig. 1. ^1H NMR spectrum of AL polymerization products in the presence of boron trifluoride (3 mass %, $T = 393$ – 400 K, 5 h; pyridine D6).

7.5–7.6, and 7.1–7.2 ppm), water (δ 8.2–8.6 ppm), and ethyl acetate (δ 3.9–4.1, 1.8–1.9, 0.9–1.1 ppm). The signals from various groups of polymer are within the range from 0.8 to 4 ppm. No signals were observed in the region of 4–7 ppm, where the peaks of olefin protons are usually observed, *i. e.* the polymerization process under the action of boron trifluoride occurs *via* opening double bonds (route (2)) almost completely.

Any biodegradation of the oligomer obtained by such microorganisms as *Saccharomyces cerevisiae*, *Streptomyces chrysomallus* and *Streptomyces lividans*, was not observed.

Anionic polymerization of AL in the presence sodium hydroxide and sodium butylate

A typical experimental technique was as it follows: into a glass ampoule with a weighed

portion of AL equal to 3 g we added sodium butylate or dust-like NaOH powder. Then the ampoule was thermostated for the period two (for ButONa) or three (for NaOH) weeks.

In the presence of crystalline NaOH the formation of a transparent highly viscous yellow-orange coloured liquid or resin from AL is observed, with a specific caramel smell. The resin is soluble in polar solvents, water-insoluble, swelling in hydrocarbons.

In the presence sodium butylate, the formation of orange viscous liquid is observed which liquid gradually passes into a light yellow resin. The resin is soluble in polar solvents, water-insoluble, swelling in hydrocarbons.

Figure 2 demonstrates the ^1H NMR spectrum of the resin sample obtained under bulk AL polymerization in the presence of crystalline NaOH at (290 ± 4) K, in air. The sample of PAL possessed the MM of 840 and the polydispersion level equal to 1.05.

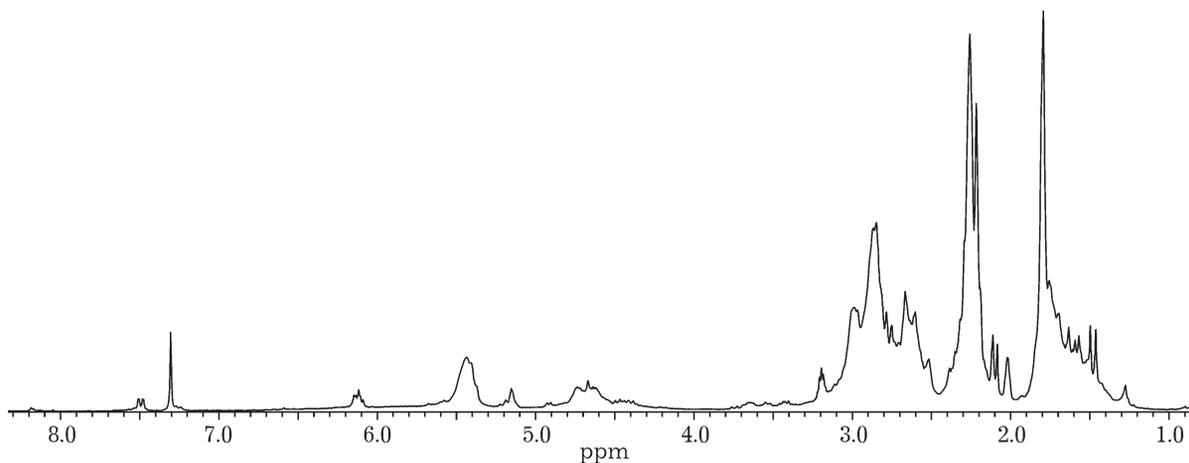


Fig. 2. ^1H NMR spectrum of AL polymerization products in the presence of NaOH at $T = (295\pm 4)$ K (210 h).

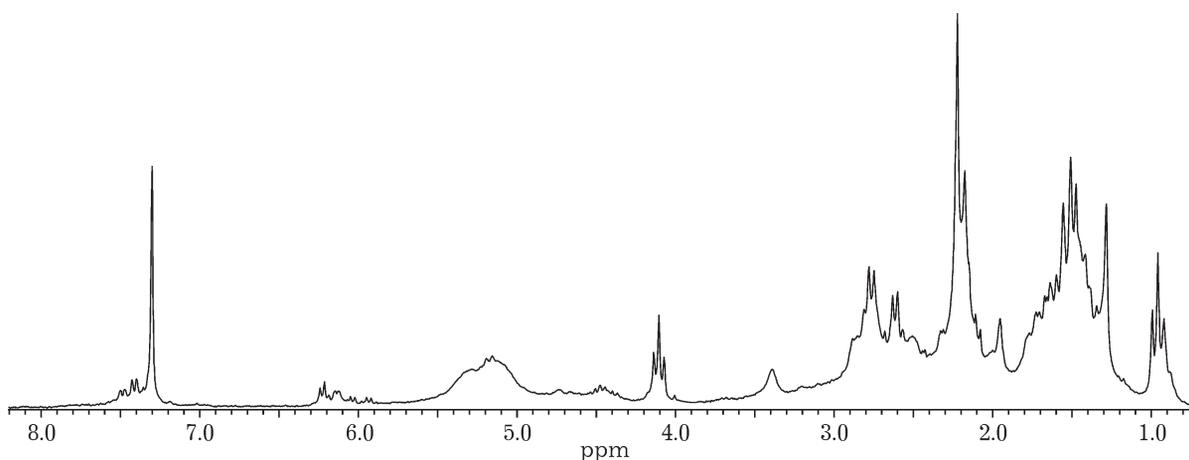


Fig. 3. ^1H NMR spectrum of AL polymerization products in the presence of sodium butylate (5 mol %) at $T = (395\pm 4)$ K (238 h).

Figure 3 presents the ^1H NMR spectrum of the resin sample obtained *via* the interaction between AL and 5 mol. % of sodium butylate at $T = (395 \pm 4)$ K. The sample of PAL exhibited the molecular mass of 1120 and the polydispersion level equal to 1.8.

The ^1H NMR spectra of the samples obtained by the polymerization in the presence of NaOH and sodium butylate, demonstrate intense signals observed within the range of 4–6 ppm, inherent in the signals of olefin and hydroxyl protons. This means that the olefin groups remain intact in the molecules of polymer, as against the products of polymerization in the presence of boron trifluoride (see Fig. 1). The fraction of signal integral intensity for olefin protons within the range of 4.0–5.6 ppm in the spectrum as a whole amounts to 0.113 and 0.134, for spectra presented in Figs. 2 and 3, respectively.

Taking into account the stoichiometry of the monomer molecule (one olefin proton among six protons in the molecule) this means that in the polymer there are 68 and 80 % fraction of olefin protons observed, counting upon their initial content in the monomer. The intermonomer bonds are formed according one of two routes such as (2) or (3); hence, one could assume that the fraction of double bonds remained in the polymer is equal to the fraction of the intermonomer polyester bonds formed. Thus, the intermonomer bonds of the polymer are formed by opening the lactone cycle (68–80 % of bonds in the polymer) and the double bond (20–32 % of bonds in the polymer), respectively.

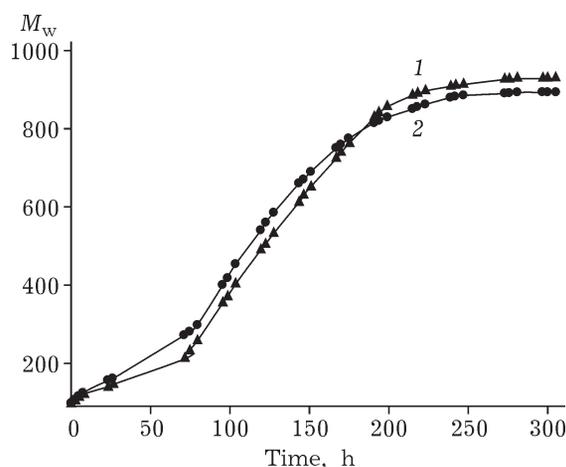


Fig. 4. Weighted average molecular mass (M_w) of PAL sample depending on time under catalyzing by sodium hydroxide (mass fraction of NaOH amounting to 5 %). T , K: 295 \pm 4 (1), 312 \pm 4 (2); M_w was estimated using viscosimetry.

Figure 4 demonstrates the weighted average MM of PAL sample under polymerization in the bulk depending on the duration of the process in the presence of 5 mass % NaOH at the temperature of 295 and 312 K. The data obtained demonstrate that the polymerization level of the polymer obtained reached under these conditions $n = 9$ –10 almost does not depend on temperature. Such weak temperature dependence could be caused by a thermodynamic process control at low values of the polymerization enthalpy.

Figures 5, 6 demonstrate the results concerning the influence of sodium butylate concentration upon the kinetics of polymerization and the MM distribution of polymers obtained at 291 K. Increasing the concentration of the initiator results in increasing the process rate, but maximum obtainable polymerization level (see Fig. 5)

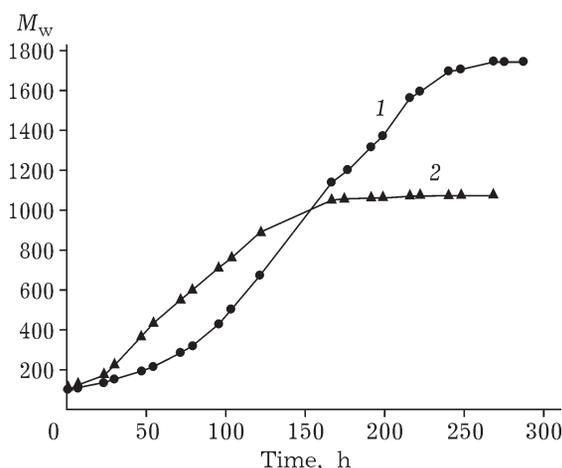


Fig. 5. Weighted average molecular mass (M_w) of PAL sample depending on time under initiation by sodium butylate ($T = (291 \pm 5)$ K). Molar fraction of ButONa, %: 3 (1), 5 (2); M_w was estimated using viscosimetry.

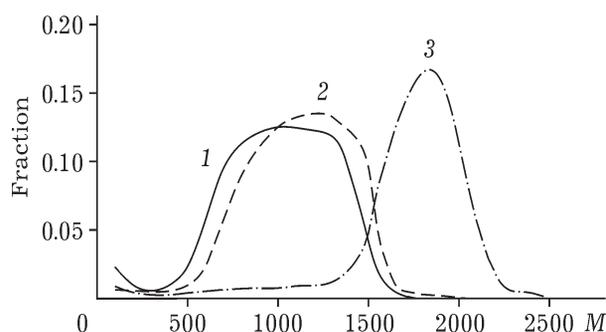


Fig. 6. Effect of sodium butylate concentration on PAL molecular mass distribution. Molar fraction of ButONa, %: 5.5 (1), 5 (2), 3 (3); M_w , Da: 986 (1), 1072 (2), 1742 (3).

TABLE 1

Results for biodegradation of obtained polymers by ray fungi and yeast

Microorganisms	Increase in mass or absorbance		Time of complete polymer degradation on mineralization must, days
	Nonmineralized substrate	Mineralization must	
<i>Saccharomyces cerevisiae</i> ,	24–30 %*	101–184 %*	5–7
set of cultures (GOST 171–81)	22–25 %**	138–143 %**	
<i>Candida parapsilosis</i> ,	n/d	52–54 %*	9–14
culture V-906	69–75 %**		
<i>Streptomyces chrysomallus</i> ,			
culture VKM 1332 N-2	n/d	50–52 %**	19–28
<i>Streptomyces lividans</i> ,			
culture TS-64	n/d	38–41 %**	24–30

Note. Here and in Table 2: n/d – not determined.

*Gravimetric determination of increasing the dry mass of microorganisms according to GOST 171–81 on the substrate based on polymer sample with $M_w = 1120$.

**Nephelometric determination of growth dynamics for microbial cultures on the substrate based on polymer sample with $M_w = 1120$.

decrease. Except for the increase in the average MM of polymer, the decrease of sodium butylate concentration results in a considerable narrowing of the MM distribution of PAL obtained (see Fig. 6). Such laws are widely distributed being natural for the processes of polymerization [20].

Polymers obtained through the AL polymerization on hydroxide and sodium butylate undergo complete or partial biodegradation during 5–30 days (Table 1). The rate of polymer biodegradation decreases in the order *Saccharomyces cerevisiae* > *Candida parapsilosis* > *Streptomyces chrysomallus* > *Streptomyces lividans*. In the same order, the amount of microorganisms determined according to the mass or *via* nephelometric technique decreases, too. The latter, to all appearance, could be connected with decreasing the bioavailability of polymers, or, otherwise, with the concentration of accessible nutrients in the system under increasing the duration of degradation. Just this results in decreasing the amount of microorganisms according to the limited resource of nutrients.

Polymerization of α -angelicalactone in the presence of sodium alcoholates in anhydrous media

Experiments in anhydrous media were carried out at 333–338 K, the duration of poly-

merization ranged from 40 to 60 min. From the resins obtained, we isolated the first representative fraction *via* the method of fractional reprecipitation from solution. Further, using the method of the capillary viscosimetry of solutions we estimated the molecular mass of the fractions obtained. The use of carefully dried reagents, an inert atmosphere and the initiation of angelicalactone polymerization by some alcoholates results in increasing the characteristic viscosity of the solutions of polyester resins obtained and in 1.5–2-fold increasing their MM at equal initiator concentrations (Table 2, Fig. 5).

It should be noted that owing to a careful dehydration of the system, a decrease of the initiator concentration in the reaction mixture can occur, which results in an abrupt increase in the MM of polymers obtained (see Table 2). Within the range of sodium butylate concentration 0.5–3 mol. % the average MM of the polyether is inversely proportional to the initiator concentration amounting to 15 000–19 000. The greatest value of MM (19 500) was obtained in the presence of isopropylate sodium.

The samples obtained undergo a partial or complete degradation in soil during 180 days; the stability of polymers grows with an increase in the molecular mass of a sample.

TABLE 2

Effect of initiator nature and concentration on the molecular mass of polyesters obtained

Initiators	Concentration, mol. %			
	0.5	1.0	3.0	5.0
Sodium butylate	15 600 (± 4000)	7700 (± 1700)	2600 (± 200)	1860 (± 200)
Sodium propylate	16 000 (± 5100)	n/d	n/d	n/d
Sodium isopropylate	19 500 (± 1800)	n/d	4900 (± 200)	n/d
Aluminium triisopropylate	15 000 (± 2000)	n/d	n/d	n/d

Block copolymerization of PAL with styrene

The following stage of the studies was directed on the improvement of PAL physico-mechanical properties *via* its copolymerization with styrene.

In the presence of styrene (1–5 mol. %), polymers with molecular mass about 200 000–500 000 (Table 3) are formed from PAL melt under the treatment by the etherate of boron trifluoride. The polymers obtained undergo a complete degradation in the environment (grey wood soil) during 140 days. The products of degradation exhibit no statistically significant toxic effect on the microflora (the experimental results concerning the death of daphnids in aqueous extracts of soil after the biodegradation of polymers and in the reference samples did not differ between each other).

Physicomechanical properties of PAL and its copolymers with styrene are presented in Table 3. According to the ultimate breaking stress and the liquid limit under stretching, the copolymers obtained surpass to a considerable

extent the State Standard (GOST) requirements for general-purpose polystyrene.

The initiation of PAL water aqueous emulsion with styrene (5–40 mass %) by azobisisobutyronitrile results in the formation of highly reactive microgels similar to the rubber/styrene phase of shock-resistant polystyrene, exhibit a strong adhesion and good fluidity, which makes them suitable for the reactive formation. Table 4 demonstrates data concerning the polydispersion properties of microgels and their glass transition temperature. The minimal polydispersion indices ($M_w/M_n = 1.2$ – 1.5) are reached at the maximal duration of polymerization (150 min) and extreme values of styrene concentration within the range under investigation (5 and 40 mass %). The glass transition temperature of microgels grows with the increase in the polymerization duration and the content of styrene in the copolymer, amounting to 157–180 °C.

After separation a solvent, the gels were subjected to the procedure of reactive formation ($t \sim 103$ – 115 °C, $P \sim 1$ – 1.2 MPa). The physico-mechanical properties of the samples formed

TABLE 3

Some physico-mechanical properties of PAL copolymers with styrene

Parameters	PAL	PAL/styrene (1–5 %)	Polystyrene of general purpose (GOST 20282–86)
Density, g/cm ³	1.10–1.12	1.15–1.16	1.05–1.07
Thermal conductivity coefficient (20–150 °C), W/(m · K)	0.30	0.24	0.082
Thermal diffusivity (20–150 °C), 10 ⁷ m ² /s	1.8	1.2	5.6
Ultimate tensile strength, MPa	–	40–65	39.2–53.9
Yield tensile strength, MPa	–	70–80	18–34
Relative lengthening at break, %	85–90	10–20	1–2
Bending stress at the deflection equal to 1.5 sample thickness, MPa	–	60–70	87–105
Molecular mass of polymer	(1–2) · 10 ³	(2–5) · 10 ⁵	–

TABLE 4

Effect of PAL/styrene emulsion copolymerization duration on the polydispersion level (M_w/M_n) and glass transition temperature ($^{\circ}\text{C}$, in brackets) for microgels

PAL/styrene, mass %	Reaction time, min			
	5	20	70	150
95/5	4.4	2.3 (108)	1.6	1.2 (136)
90/10	3.9	2.5 (110)	1.6	1.4 (132)
80/20	6.2	4.1 (117)	3.8	3.5 (140)
70/30	6.5	5.8 (133)	4.4	4.1 (152)
60/40	5.8	4.3 (157)	2.6	1.5 (180)

are to a considerable extent changed depending on the structure and conditions of the formation process. The samples formed during 60 days undergo partial degradation by soil microorganisms. The products of degradation exhibit no statistically significant toxic effect on the microflora (the killed daphnids in aqueous extracts of soil after the biodegradation of polymers and in the reference samples did not differ between each other).

CONCLUSION

The experiments carried out demonstrate that AL (rather inert monomer) under suitable conditions is polymerized both *via* opening the lacton cycle, and through the double bond [21–23]. The most high molecular mass poly lactones obtained (molecular mass of 15 000–20 000) partly or completely degrade in soil during 180 days. The polymers with polyolefin structure obtained almost do not yield to biodegradation by ray fungi and yeast, whereas poly lactones with similar molecular mass (800–1000) completely degrade under the action of these microorganisms during 5–30 days. These results

demonstrate that the oligomeric poly lactones obtained could be used as block copolymer resin for giving biodegradation properties to polymers those exhibit no such properties: polystyrene, polycaprolactam, polyester resins, *etc.*

Indeed, polyangelicolactone copolymerization with styrene results in obtaining copolymers yielding to biodegradation by soil microorganisms within a half-year and exhibiting physico-mechanical properties, close to those required for the general purpose polystyrene.

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