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Polyesterification of alpha-Angelicalactone

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alpha-Angelicalactone can be polymerized by two ways: as the substituted ethylene and as lactone. Polyesters of alpha-angelicalactone are obtained on alkali based catalysts. The obtained polymers are light yellow resins or solid, water-insoluble and soluble in polar organic solvents. Molecular weight of the obtained polymers is up to 2000 amu. The structure of the polymers is studied by ^{1}H NMR spectroscopy. It is shown, that the part of polyester intermonomeric bond is more than 68 %.
The obtained polymers are exposed to full biodegradation by microorganisms Sacharomices cerevisae during 5 - 15 day, and by Streptomyces lividans and Streptomyces chrysomallus - during 20 - 30 day.

Keywords: angelicalactone, anionic polymerization, polyangelicalactone, biodegradation.

Introduction

The amount of production of naturally-indestructible petrochemical-based polymers and plastics are immense and annually increase by approximately 28 million tons. At that the major part of these plastics is stored on landfills, since their recycling in developed countries is just amount to 16-20 %. Now amounts of production of synthetic plastics have reached 200 million tons per year. Projects of possible methods of chemical plastics re-use are non-optimistic. Therefore the problem of a "polymeric dust" solving is to develop of the new polymers able to natural degradation to the harmless components. The amount of degradable synthetic polymer in use today is negligible, probably under 1%. This could conceivably be increased to a few percent, which would have a minor effect on landfill growth but which could be important if applied to critical situations [1-3].

α-angelicalactone (5-methyl-2(3H)-furan-1-one) is attractive substance to research of new material syntheses, therefore it can be obtained from renewable natural materials (I). The molecule of α-angelicalactone has two polymerizable groups: an ester group is joined to a double bond. Thus, there are two possible ways of polymerization: - disclosing of an olefinic linkage with formation of a polyfuranone (II) and disclosing of the lactone cycle with formation of a polyester (III).

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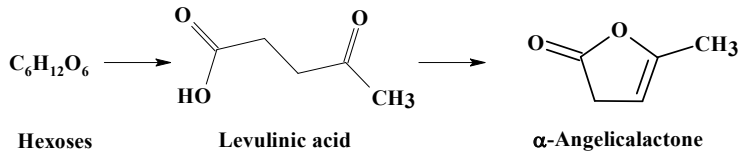
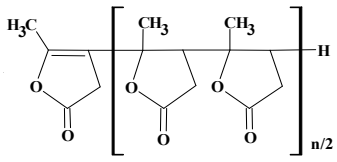
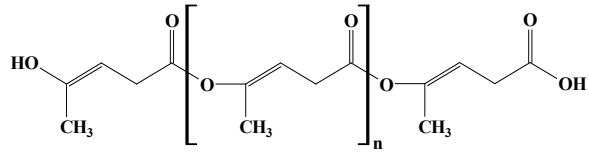


Hexoses Levulinic acid α-Angelicalactone (I)



(II)



(III)

Disclosing of double bond is carried on in presence of Lewis acids with the formation of oligomeric (n=2-8) polyfuranone [4,5].

Polyesterification of angelicalactone is the most interesting, but data on this problem are absent [6,7]. Products of such reactions can be biodegradable or biologically compatible [7-9]. Inorganic and organic bases [7,8], organometallic compounds [9] are preferable catalysts for the lactone polymerization.

In this paper polyesterification of alpha-angelicalactone and polyesters ability to biodegradation are studied.

Experimental

alpha-Angelicalactone was obtained by vacuum still of a levulinic acid (~25 mmHg, 340-345 K) and purified by fractional melt crystallization. A levulinic acid was synthesized according to [10]. Sodium butylate was synthesized according to [11]. Solvents (dioxane, ethyl acetate, diethyl ether, dichloroethane, n-butanol, and benzophenone) were purified by fractional distillation in vacuum.

Molecular weights of the obtained polymers estimated by viscosimetry (Ostwald viscosimeters, diameter 0.12 and 0.56 mm, benzophenone) and cryoscopy (benzophenone).

The chain-length distribution was determined by phase-reversal chromatography. The column is Nova-Pak CIS (Waters Corporation, USA); sorbent is octadecyl-coupled silica gel; vaporizing light scattering detection device, model 500 (Alltech Corporation, USA); eluent – acetonitrile/ tetrahydrofuran (MeCN/THF = 58/42), flow rate 1 ml/min.

Products purity was confirmed by gas-liquid chromatography and ^{1}H NMR spectroscopy (spectrometer Bruker DPX-200W). The NMR spectroscopy also has been involved for research of polymers structure.

Biodegradation ability of the obtained polymers was estimated by liveweight gain of cultures of microorganisms *Sacharomices cerevisae*, *Streptomyces chrysomallus* and *Streptomyces lividans* and by observing of polymers mass decreasing.

Polymerization of alpha-angelicalactone by the sodium butylate. – To three spot series of 3 g (~0,031 mol) of *a*-angelicalactone were added: (1)152 mg (~$1{,}7\times10^{-3}$ mol), (2) 138 mg (~1,6 ⇔ 10^{-3} mol), (3) 83 mg (~9,3 ⇔ 10^{-4} mol) of the sodium butylate. Samples in glass ampoules were placed to thermostatic system at 291±5 K up to two weeks. The viscous yellow polymer layer was washed by decantation with several portions of diethyl ether, and freed of volatile matter by heating slowly (one and a half hours) to 80° at 2 mmHg. There remained 2.8 – 2.94 g. of a slightly yellow solid, tacky, but showing no cold flow. It was readily soluble in acetone, dioxane, ethyl alcohol and butyl alcohol, ethyl acetate,

slowly soluble in aqueous sodium hydroxide, insoluble in water, ether, and benzene.

Mol. wt. (amu): (1) 986, (2) 1072, (3) 1742.

Fig. 1 shows ^{1}H NMR spectrum of a sample of the resin obtained at interaction of angelicalactone with 5 mol. % of sodium butylate at T~395 K. The sample had molecular weight 1072, polydispersity - 1,8.

The molecular weight grow are presented at Fig. 2.

The chain-length distribution of polyangelicalactone depends on catalyst concentration. The dependence is presented on Fig. 3.

Polymerization of alpha-angelicalactone by the sodium hydroxide. – 15 mg of the sodium hydroxide powder were added to two spot series of 3 g (~0,031 mol) of *a*-angelicalactone. The samples in glass ampoules were placed to thermostatic system at: (1) 295 ± 4 K, (2) 312 ± 4 K, up to three weeks. Then, the lactone had polymerized to a very viscous orange liquid. Polymer layer was washed by same method as sodium butylate catalyzed polymer. There remained up to 2.6 g of a very viscous yellow liquid. The liquid had

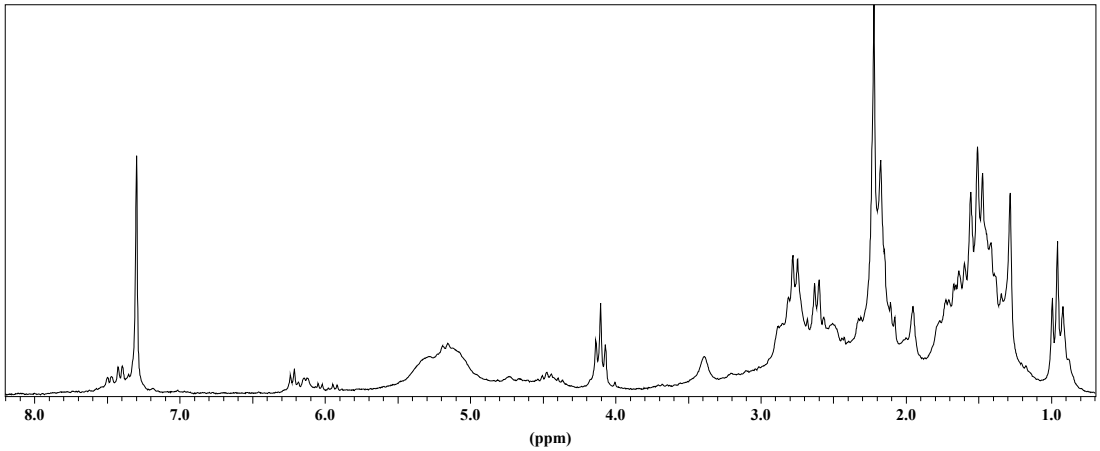


Fig. 1. The ^{1}H NMR spectrum of a product of angelicalactone polymerization in the presence of sodium butylate (5 mol. %) at T = 395 K (238 hours)

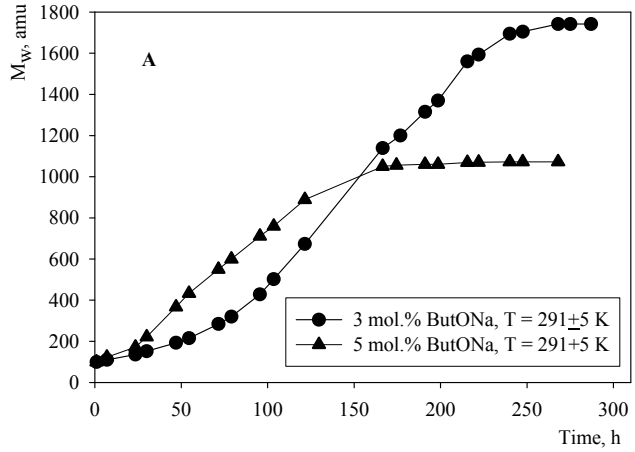


Fig. 2. Time dependence of average molecular weight of the sodium butylate catalyzed polymer

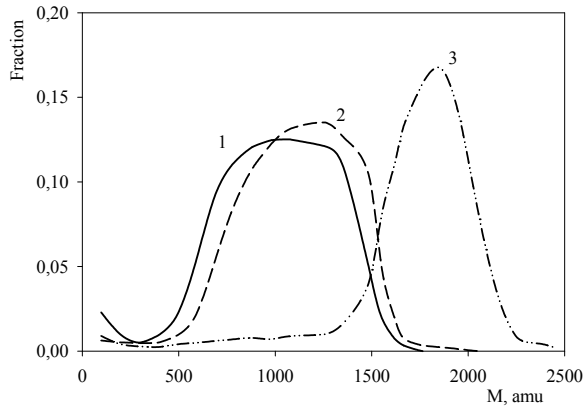


Fig.3. Chain-length distribution of polyangelicalactone in the presence of catalysts: 1 – 5,5 mol.% ButONa (Mw=986 D); 2 – 5 mol.% ButONa (Mw=1072 D); 3 – 3 mol.% ButONa (Mw=1742 D)

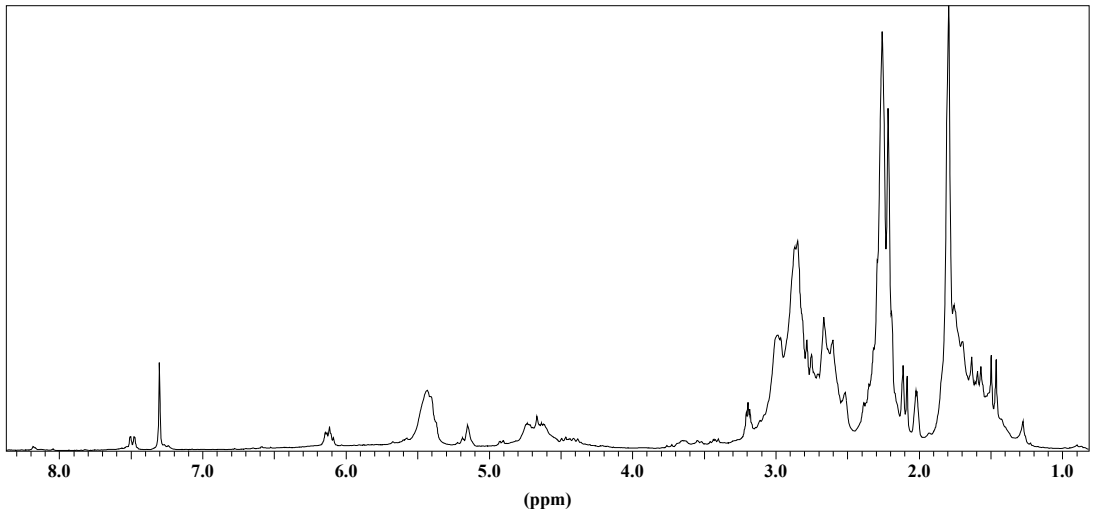


Fig. 4. The ^{1}H NMR spectrum of polymerization products of α-angelicalactone at presence NaOH at T = 290 K (210 hours)

the same solubility characteristics as the sodium butylate catalyzed polymer.

Mol. wt. (amu): (1) 928, (2) 893.

Fig. 4 shows the ^{1}H NMR spectrum of a sample of the polymer obtained at polymerization angelicalactone in the presence of sodium hydroxide at T~290 K. The obtained substance has molecular weight 893 and size of polydispersity 1,05.

The grow of molecular weight of the sodium hydroxide catalyzed polymer are presented in Fig. 5.

Estimation of polyangelicalactone biodegradation ability. – Microbiological culture (0,5 g, ~10^{7}-10^{8} colony-forming units) was added to a shot of polymer (3 g) and 2 ml of the water solution containing 1,45 M of sodium chloride, 1,19 M of ammonia phosphate , 0,48 M of magnesium sulphate, or 2 ml of distilled water for estimation of polymer biodegradation in non-mineralized medium. The prepared samples were maintained at 308±1 K during 5 - 30 day. Completeness of polymer degradation was estimated by full dissolution of resin samples. The

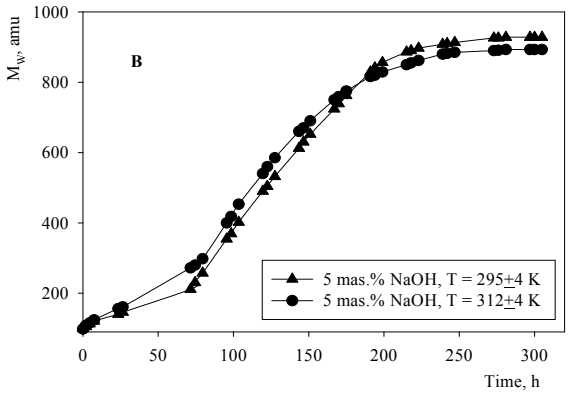


Fig. 5. Time dependence of average molecular weight of the sodium hydroxide catalyzed polymer

Table 1. Results of biodegradation of the obtained polymers by actinomycetes and yeast

Spieces of microorganisms	The increment of weight* or optical density**		Time of full degradation, day
	A	B	
Sacharomices cerevisae[1]	24 -30 %* 22-25%**	101-184 %* 138-143%**	5-7
Streptomyces chrysomallus[2]	-	50-52%**	19-28
Streptomyces lividans[3]	-	38-41%**	24-30

1 - a set of strains (GOST 171-81); 2 - strain VKM 1332 H-2; 3 - strain TS-64.
* - gravimetric determination of an incremental value of dry weight of microorganisms in accordance with GOST 171-81 on substrate from a sample of polymer with Mw=1120 amu.
** - nefelometric determination of dynamics of propagation of microbiological cultures on substrate from a sample of polymer with Mw=1120 amu.

microorganisms liveweight gain was estimated by increasing of suspended cultures dry weight and culture liquids optical density (λ= 540 nm, cell thickness = 1 cm, nephelometric method).

These experiments have shown, that the obtained polymers are exposed to full biodegradation by microorganisms *Sacharomices cerevisae* during 5 - 15 day, and *Streptomyces lividans* and *Streptomyces chrysomallus* - during 20 - 30 day (Table 1).

Discussion

From the results obtained using these catalytic systems, the fist time obtained polyesters of alpha-angelicalactone [12] had a low values of molecular weights, theirs polymerization degree reaches values n = 9 - 20, and has tendencies to increase at catalyst concentration and temperatures decreasing. Assessed value of polymerization degree is

$$n = k\frac{[M]^0}{[cat]^0},$$

where $[M]^0$ is initial monomer concentration, $[cat]^0$ - initial catalyst concentration, k - proportional coefficient. k is temperature and reaction conditions depending and consist of 0.58 to 1.74 and, probably, up to 2 under low temperature (about 200 K).

Signals of olefinic protons in ^{1}H NMR spectra of the obtained samples are brought into correlation with intensive signals at 4 - 6 ppm. Integrated intensity of signals of area 4,0 - 6 ppm is come to 0,113 and 0,134 for spectra of polymerization products on sodium hydroxide and sodium butylate, accordingly. Therefore, 68 and 80 % initial contents of olefinic protons in

monomer are kept in polymer. Thus, under action of the basic catalysts intermonomeric bonds of polymer are formed basically by disclosing the lactone cycle (68 - 80 % of bonds in polymer).

Conclusions

The polymer prepared by the action of basic catalysts on alpha-angelicalactone has been shown to be a polyester having the "head to tail" structure. The part of polyester intermonomeric bonds in the obtained products of polymerization reaches 68 - 80 %. The obtained polymers give in to biodegradation by the microorganisms during 5 - 30 days.

Key properties of homopolyesters from angelicalactone are its biodegradability, possible biocompatibility, and its manufacture from renewable resources. Primary application area in which these features meet some needs is medical: polyangelicalactone's biocompatibility coupled with its slow hydrolytic degradation lead to potential in reconstructive surgery and controlled release fields.

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