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Biodegradation of Polymers Based on Styrene and Polyangelicalactone

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Abstract. Polyangelicalactone-*graft*-polystyrene copolymers (PAL-*graft*-PS) were obtained through cationic polymerization. The resulting copolymers were completely destroyed when incubated in gray forest soil over 28 weeks. Individual strains of fungi destroyed the copolymer partially within 13 weeks; the most active among the studied cultures was *Leptographium sp.* The biodegradation products of copolymers do not statistically have a toxic effect. The obtained results show that the modification of polystyrene (PS) with the impurities of polyangelicalactone (PAL) gives them biodegradation abilities and does not worsen the properties of the copolymers.

Keywords: biodegradation; copolymerization; polystyrene; *α*-angelicalactone; polyangelicalactone; poly[oxidiyl(4-methyl-1-oxobut-3-en-1,4-diyl)]; poly[oxidiyl(4-methyl-1-oxobut-3-en-1,4-diyl)]-*graft*-poly(1-phenylethylene).

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Биодеградация полимеров на основе стирола и полиангеликалактона

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Аннотация. Получены привитые сополимеры стирола с полиангеликалактоном (PAL-*graft*-PS) методом катионной полимеризации. Установлено, что сополимеры полностью разрушаются при инкубации в серой лесной почве в течение 28 недель. Отдельные штаммы грибов частично разрушали сополимер в течение 13 недель; среди изученных культур наиболее активна *Leptographium sp.* Продукты биоразложения сополимеров и блок-сополимеров статистически не обладают токсическим действием. Полученные результаты показывают, что модификация полистирола (PS) примесями полиангеликалактона (PAL) придает им способность к биоразложению, не ухудшая свойства сополимеров.

Ключевые слова: биоразложение, сополимеризация, полистирол, ангеликалактон, полиангеликалактон, поли[оксидил(4-метил-1-оксобут-3-ен-1,4-диил)], поли[оксидил(4-метил-1-оксобут-3-ен-1,4-диил)]-прив-поли(1-фенилэтилен).

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Introduction

An urgent problem of modern civilization is determining how to give polymer materials the ability to biodegrade into safe, nontoxic compounds in the environment [1–4]. One method is to obtain copolymers with monomers or polymers that have this ability.

One new biodegradable polymer is polyangelicalactone (poly[oxidiyl(4-methyl-1-oxobut-3-en-1,4-diyl)], PAL), a product of the anionic polymerization of α-angelicalactone (5-methylfuran-2(3H)-one, AL). α-Angelicalactone (lactone of levulinic acid) is obtained from renewable raw materials, fructose, cellulose, and other carbohydrates. The most interesting reactions are the polymerization of AL with opening of the lactone ring, which occurs in the presence of sodium hydroxide, sodium butylate [5, 6], and stannous octoate ($Sn(Oct)_2$) [7]. The products of such reactions have the ability to biodegrade [5–9].

Saturated five-membered lactones are not usually subjected to ring-opening polymerization (ROP) [13], but a double bond in the cycle can activate this polymerization. Therefore, opening the lactone cycle to form polyester is allowed by thermodynamics [10].

Low-molecular PAL samples (M_w 800–1100) undergo almost complete biodegradation via the microorganisms *Candida parapsilosis* and *Saccharomyces cerevisiae* within 5–15 days and through *Streptomyces lividans* and *Streptomyces anulatus* within 20–30 days [5, 6]. Higher molecular weight PAL samples (M_w 15,000–19,000) undergo partial or complete degradation in the soil in 180 days, and the stability of the polymers increases with an increase in their molecular weight [6].

Polystyrene (PS) is a large-scale industrial polymer. It is widely used, for example, to manufacture disposable tableware. This increases the amount of polymeric waste dispersed throughout the environment [1]. The problem of environmental pollution caused by these wastes can be solved by producing PS biodegradable modifications.

Copolymers with molecular weights of 200,000–500,000 were obtained through the reaction of melted PAL with styrene (1–5 mol%) in the presence of boron trifluoride diethyl etherate as a catalyst. Such copolymers underwent complete biodegradation in gray forest soil in 140 days [9]. The copolymerization products of AL and PAL with styrene (St), caprolactam, ethylene terephthalate, and methyl methacrylate were shown to be susceptible to complete or partial biodegradation in the forest soil or in composting plant wastes under conditions of anaerobic or aerobic digestion [8]. The emulsion polymerization of polyangelicalactone with styrene was also carried out. High-impact biodegradable block copolymers (M_w 40,000–1,000,000) containing 5–40 wt% of styrene were prepared [12].

A wide range of the grafted copolymers were synthesized and studied recently [13]. The goal of this work is to study the biodegradation of the polyangelicalactone-*graft*-polystyrene (PAL-*graft*-PS) with a wide range of compositions.

Experimental part

PAL was obtained via ring opening polymerization in a solution in tetrahydrofuran in the presence of aluminium isopropoxide and benzophenone ketyl-Na [13]. For this study, PAL with M_w ~6000 g × mol^{-1} was used. Cationic St polymerization, and PAL grafting with St was performed in the presence of boron trifluoride etherate as the catalyst [13].

Biodegradation of the copolymer via pure fungal cultures was studied on a sample PAL-*graft*-PS [20:80]. The fungi cultures *Leptographium sp.*, *Ophiostoma sp.*, *Aureobasidium pullulans*, and *Tricho-*

derma harzianum (collection of the Sukachev Institute of Forestry at the Russian Academy of Sciences) were used as destructors. For the liquid culture medium preparation, the diluted nonhopped beer wort (the concentration of sugars was 1 °Bx) were sown with blocks (diameter 6 mm) cut from the colony of the corresponding fungi culture on the wort agar and were incubated at 24 °C for three days. The polymer film pieces with an area of 1,5–2,5 cm^2 and thickness 0,4–1,0 mm were decontaminated by boiling in a water bath for 30 minutes and then exposed in stationary liquid culture medium at 24 °C within 13 weeks, stirring manually once a week. Twin 60 (100 mg/L) was added to several samples during sowing, which is known to have a positive effect on the rate of microbial decomposition of synthetic polymers [14]. All operations were performed in a sterile manner.

Biodegradation of the copolymers in soil was studied on samples of gray forest soil (Greyic Phaeozems (Albic), WRB, 2006). Twenty samples of soil with a total weight of 10 kg from horizon A at a depth of 0–5 cm were collected in continental subboreal forests (mixed forests with a predominance of *Pinus sylvestris*) near the city of Krasnoyarsk, Russia (N 55° 59’ 26” E 92° 42’ 15”, 250–270 m a.s.l.). All sample preparation operations were performed under sterile conditions. All samples were combined and thoroughly mixed. The soil samples were air-dried and sieved with a 2 mm sieve. Clods were crushed and sieved again. Soil of the following composition was used for the experiments: moisture content, 32,4 ± 2,6 wt%; pH of water extract, 5,2 ± 0,3; humus content, 4,3 wt%; total organic carbon content, 31,2 ± 0,2 mg/g; total nitrogen content, 2,1 ± 0,6 mg/g.

In a sterile chamber, polymer samples 5 × 5 × 1 mm in size with a weight of about 25 mg and 15 g samples of carefully dried soil were placed in 45 mL glass tubes. The system was wetted via microdrip irrigation with a sterile synthetic nutrient medium to maintain 100 % air humidity. Synthetic nutrient medium was as follows: K_2HPO_4, 7,0 g; KH_2PO_4, 0,3 g; $MgSO_4 \times 7H_2O$, 0,1 g; $(NH_4)_2SO_4$, 1,0 g; sodium citrate trihydrate, 0,5 g; MgO, 0,1 g, $FeCl_3$, 0,054 g; $ZnSO_4 \times 7H_2O$, 0,014 g; $MnSO_4 \times 4H_2O$, 0,011 g; $CuSO_4 \times 5H_2O$, 0,0025 g; $CoSO_4 \times 7H_2O$, 0,0028 g; H_3BO_3, 0,0006 g; $Na_2MoO_4 \times 2H_2O$, 0,0049 g; distilled water up to 1 l). The system was thermostated at 24 °C for 28 weeks.

Every fourth week, one test tube of each copolymer sample was taken out. The polymer samples were then washed with distilled water to remove any residual soil particles and placed in a desiccator to achieve a constant weight. After the mass measuring, the sample did not return to the experiment.

The next stage of the study, involving a statistical estimation of the toxicity of the polymer degradation products, was carried out using water extracts of the cultivated masses. The cultivated masses were dispersed in distilled water (45 mL of water per sample) using a mechanical disperser over 3 minutes and then filtered. Then, 5 mL of synthetic nutrient medium (0,1 g/L NaCl; 0,01 g/L KCl; 0,01 g/L $MgSO_4$; 0,01 g/L $CaCl_2$; 0,02 g/L $NaHCO_3$) was added to the filtrates, boiled for 5 min, and then cooled to room temperature. *Stylonychia mytilus* (Ehrenberg) and *Daphnia magna* (Straus) cultures were used as the test organisms (Table 1). *Stylonychia* cultivations in the obtained media were performed on the multicuvette cultivation device KVM-05 (LLC Europolitest). *Daphnia* expositions were performed on the device for exposing crustaceans UER-03 (LLC Europolitest). A toxicity assessment of the mortality, immobility, and young production of the test objects was carried out by measuring the number of test objects via direct counting.

Identification of the species of fungi present in the cultivated masses was performed using the four culture media Czapek agar, Starch-and-ammonia agar, Waksman agar, Wort Agar [15]. All media were sterilized by autoclaving at 121 °C for 30 minutes. After sterilization and before sowing of Wort

Table 1. Test organisms and a brief methodology of the mortality tests

Species (test)	Organism age	Feeding organisms	Exposure time	Number of duplicate runs	Test endpoints
Stylonychia mytilus (acute)	One day – exponential growth	*Saccharomyces cerevisiae*	1 h	64	Mortality
Daphnia magna (acute)	≤ 24 h old – age-synchronized culture	None	48 h	64	Mortality
Daphnia magna (chronic)	≤ 24 h old – age-synchronized culture	*Saccharomyces cerevisiae*, *Chlorella vulgaris*	28 days	16	Mortality, immobility, young production

Agar and Czapek agar, 0,4 % (by volume) of concentrated lactic acid was added to the molten agar in a sterile manner.

Samples of cultivated masses (1 g) were transferred to 50 mL sterile test tubes and then diluted with distilled water to prepare dilutions of 10^{-1} to 10^{-4}. The next stage involved application of the prepared dilution to a Petri dish with a culture medium. The plates prepared in this manner were then incubated for 72 hours at a temperature dependent on the type of substrate used. Analyses of the qualitative composition were performed based on the macro- and microscopic characteristics using selected items from the taxonomic literature [16–19].

Results and discussion

The copolymers were synthesized according to scheme (Fig. 1) [13].

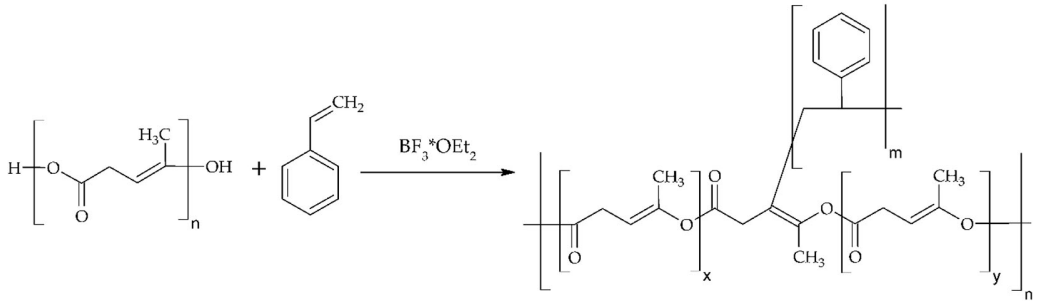

Fig. 1. Scheme of PS and PAL grafting

Biodegradation of the obtained copolymers by pure fungi cultures

The polymer degradation rates caused by individual strains are known to be slower compared to the degradation rates caused by the natural colonies of various microorganisms in many cases. Over 3 months of incubation, the rectangular pieces of film in the cultures were overgrown with the mycelia of fungi and did not lose their shape. In the cavities formed on the surface of the film, clusters of dark mycelia *Leptographium sp.* and *T. harzianum* were observed. The data presented in Table 2 show that the maximum weight loss of the samples observed in the experiments exceeded 30 % (*Leptographium*

Table 2. Weight loss (%) of PAL-*graft*-PS [20:80] samples aged in liquid fungi strains for 3 months

	Fungi species			
	Aureobasidium pullulans	*Trihoderma harzianum*	*Ophiostoma* sp.	*Leptographium* sp.
Culture medium	14,6	23,4	26,0	34,3
Culture medium with Tween 60	-	-	37,1	25,5

sp. culture). The level of degradation after 3 months was about the same in the cultures of *T. harzianum* and *Ophiostoma sp.* The least active film destruction was observed in the culture of *A. pullulans*.

The high degree of film destruction in the *Leptographium sp.* culture may be associated with the dark pigmentation of the culture. Dark-colored fungi with melanized mycelia are known to be more resistant to adverse environmental factors, including technogenic sources of pollution, such as unsaturated hydrocarbons and heavy metals [20].

The addition of Tween 60 to the cultivation media of the fungi likely acted selectively. Traces of Tween 60 increased weight loss of the copolymer caused by the *Ophiostoma sp.* culture compared to the variant of biodegradation without Tween 60. However, the rate of copolymer biodegradation caused by the *Leptographium sp.* culture decreased in the medium with Tween 60.

Fig. 2 shows micrographs of the original and biodegraded copolymer samples containing 20 wt% of PAL. The initial polymer was a two-phase system featuring spherical globules 5–40 micrometers in size (Fig. 2a). Such globules were dissolved when treating the sample with an aqueous alkali (Fig. 2b); hence, they were mainly ester polymers of AL.

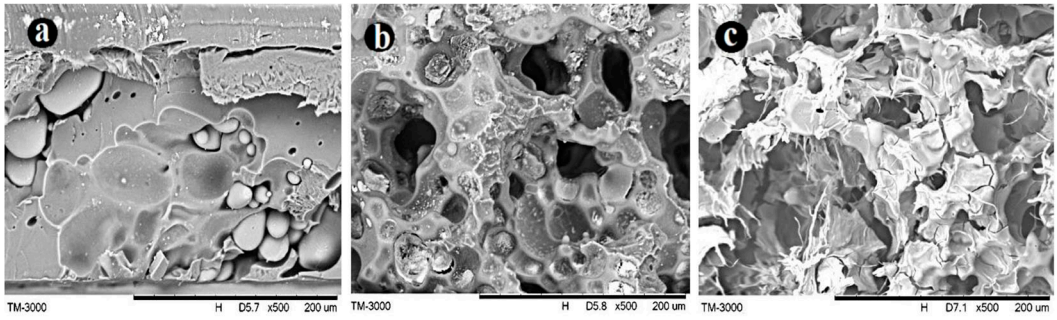

Fig. 2. Micrographs of the original copolymer PAL-*graft*-PS [20:80] (a), hydrolyzed with an aqueous solution of NaOH (b), and biodegraded (*Leptographium sp.*) samples (c)

Biodegradation of the copolymer (Fig. 2c) led to deeper and more inhomogeneous destruction than degradation via copolymer hydrolysis using the NaOH solution (Fig. 2b). Moreover, traces of biodegradation were clearly visible in the polystyrene matrix, the first of which were the matrix cracks. It should be noted that when the content of PAL in the polymer was 20 %, the loss of its mass in the process of biodegradation exceeded this value and reached 31 %-37 % (Table 3). Thus, the obtained results show that biodegradation via the *Leptographium sp.* strain partially destroys the PS.

Biodegradation of the obtained copolymers in the soil

Table 3 shows the results of the biodegradation of PAL-*graft*-PS in the gray soil. All the copolymer samples, starting from 2 wt% PAL content, were fragmented in 28 weeks.

The first stage of copolymer biodegradation was observed by the weight method after four weeks for the samples containing 80–100 wt% of PAL (a lost weight of 4–6 wt%). The St homopolymer was much more stable under the conditions of biodegradation and lost only 0.02–0.07 wt% of its mass after 20–28 weeks of the process. Mechanical destruction of the copolymers with a high content of AL (≥ 50 wt%) occurred after weight loss of approximately 10 %. The copolymers with a low content of AL (≤ 30 wt%) were mechanically destroyed after weight loss of 3–4 %, and a 4–12-week induction period of weight loss was observed for these copolymers.

Microbiological tests of the organic conglomerate samples after destruction of the copolymers were also performed. In these tests, we found micromycetes, *Phanerochaete spp.*, *Acremonium spp.*, *Aspergillus spp.*, *Clonostachys spp.*, *Fusarium spp.*, *Mucor spp.*, *Penicillium spp.*, *Trichoderma spp.*, *Ulocladium spp.*, and *Umbelopsis spp.*

A statistical estimation of the acute toxicity of the aqueous extracts from the biodegradation products was carried out using *Stylonychia mytilus* and *Daphnia magna* as test organisms (Table 4). Water extracts from the copolymer biodegradation mass at a concentration of 500 mg/l did not show a toxic effect in terms of mortality for the test objects since the average mortality of *Stylonychia* and *Daphnia* does not exceed 10 % [21–22]. According to terms and conditions of [21–22], such level of

Table 3. Weight loss of PAL-*graft*–PS samples during incubation in soil (wt%)

Sample	4	8	12	16	20	24	28
PS	0	0	0	0	0,02	0,03	0,07
PAL-*graft*-PS [2:98]	0	0	0,05	0,52	1,87	2,92	F
PAL-*graft*-PS [3:97]	0	0	0,05	0,57	2,50	4,01	F
PAL-*graft*-PS [5:95]	0	0	0,06	0,89	3,66	5,98	F
PAL-*graft*-PS [10:90]	0	0,01	0,16	1,62	4,79	F	-
PAL-*graft*-PS [20:80]	0	0,15	0,71	3,18	F	-	-
PAL-*graft*-PS [30:70]	0.02	0,53	1,26	4,49	F	-	-
PAL-*graft*-PS [40:60]	0.50	1,12	2,07	6,04	F	-	-
PAL-*graft*-PS [50:50]	1.10	2,01	4,76	8,77	F	-	-
PAL-*graft*-PS [60:40]	1.82	3,23	7,03	11,12	F	-	-
PAL-*graft*-PS [70:30]	2.66	4,06	9,75	F	-	-	-
PAL-*graft*-PS [80:20]	4.04	6,39	12,82	F	-	-	-
PAL-*graft*-PS [90:10]	4.22	8,34	F	-	-	-	-
PAL-*graft*-PS [95:5]	4.56	9,42	F	-	-	-	-
PAL-*graft*-PS [97:3]	6.02	9,87	F	-	-	-	-
PAL-*graft*-PS [98:2]	5.78	9,72	F	-	-	-	-
PAL	6.20	10,30	F	-	-	-	-

F – fragmented.

Table 4. Dependence of the statistical assessment of acute toxicity of the water extracts from the products of the biodestruction of PAL- *graft* -PS copolymers from the AL content in the copolymers

Sample	*Stylonychia mytilus*		*Daphnia magna*	
	Mortality (1 h), %	Standard deviation	Mortality (48 h), %	Standard deviation
PS	3.57	1.44	1.75	0.68
PAL-graft-PS [2:98]	3.81	1.54	1.35	0.87
PAL-graft-PS [3:97]	4.21	1.50	5.20	1.05
PAL-graft-PS [5:95]	2.19	1.39	1.40	0.90
PAL-graft-PS [10:90]	3.48	1.45	2.15	0.96
PAL-graft-PS [20:80]	2.40	1.10	3.30	1.33
PAL-graft-PS [30:70]	3.67	1.80	2.76	1.52
PAL-graft-PS [40:60]	2.78	1.28	2.62	1.49
PAL-graft-PS [50:50]	3.30	1.34	2.39	1.38
PAL-graft-PS [60:40]	3.63	1.25	2.36	1.46
PAL-graft-PS [70:30]	5.38	1.15	2.76	1.27
PAL-graft-PS [80:20]	3.63	1.26	2.16	1.37
PAL-graft-PS [90:10]	3.23	1.30	2.65	1.48
PAL-graft-PS [95:5]	2.69	1.24	2.00	1.38
PAL-graft-PS [97:3]	2.74	1.26	1.91	1.29
PAL-graft-PS [98:2]	2.93	1.35	2.32	1.49
PAL	4.00	1.60	2.50	1.55
Soil extract (control)	1.46	0.92	0.52	0.34
Water (control)	0.56	0.12	0.3	0.16

mortality corresponds to the toxicity lack. We observed only a few rare cases of the mass spontaneous death of test subjects, likely due to the high concentrations of toxins of microorganisms involved in the biodestruction of the polymers.

Conclusions

Series of polyangelicalactone-*graft*-polystyrene copolymers were obtained through cationic polymerization earlier [13]. Increasing the portion of styrene units in the copolymers improved the strength properties and increased fragility. Increasing the PAL content in the copolymers increased the elasticity of the materials obtained.

Biodegradation of the PAL-*graft*–PS [20:80] copolymer using pure fungi cultures (*Leptographium sp.*, *Ophiostoma sp.*, *Aureobasidium pullulans*, and *Trichoderma harzianum*) for 13 weeks led to the partial or complete degradation of the polyangelicalactone globules and partial destruction of the polystyrene matrix. This biodegradation led to weight loss of the polymer composition up to 37 wt%, and this value exceeded the content of AL in the polymer (20 wt%). The most active destructor among the studied cultures was *Leptographium sp.* In the process of incubating the composition samples in gray forest soil, a succession of soil microorganisms appeared on the surfaces of the samples. Under the action of the enzyme systems of these microorganisms, the incubated samples of the polymer compositions were mechanically destroyed within 28 weeks. The resulting water-soluble

biodegradation products did not statistically demonstrate toxic effects according to mortality tests with the *Stylonychia mytilus*.

Thus, the resulting polyangelicalactone-*graft*-polystyrene copolymers have physical and mechanical properties corresponding to the requirements for general-purpose PS [13] and can completely biodegrade in gray forest soil after 28 weeks.

There are two main problems in polymer biodegradation. The first is mechanical destruction of the macrosamples, and the second is microplastic mineralization down to CO_2 and H_2O. The obtained results show that the modification of PS with impurities of PAL or AL can at least solve the first problem without worsening the properties of the copolymers.

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