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## Radical Copolymerization of Styrene and $\alpha$ -angelicalactone: Synthesis and Properties of the Obtained Copolymers

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**Abstract.** Biodegradation ability of synthetic polymer materials is an urgent problem of modern ecology situation. A known new biodegradable polymer is polyangelicalactone (PAL). In this paper, styrene- $\alpha$ -angelicalactone copolymers were obtained by radical polymerization. The resulting copolymers have physical and mechanical properties similar to those of polystyrene and its graft-copolymers with PAL. Both they were mechanically destroyed when incubated in gray forest soil over 28 weeks. The obtained results show that the modification of polystyrene with the impurities of  $\alpha$ -angelicalactone does not worsen the mechanical properties of the copolymers but instead gives them biodegradation abilities.

**Keywords:** copolymerization; styrene;  $\alpha$ -angelicalactone, biodegradation.

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## Радикальная сополимеризация стирола и $\alpha$ -ангеликалактона: синтез и свойства полученных сополимеров

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**Аннотация.** В настоящей работе получены сополимеры стирола и  $\alpha$ -ангеликалактона методом радикальной полимеризации. Полученные сополимеры имеют физико-механические свойства, аналогичные свойствам полистирола и его привитых сополимеров с полиангеликалактоном. Оба полимера механически разрушаются при инкубации в серой лесной почве в течение 28 недель. Полученные результаты показывают, что модификация полистирола примесями  $\alpha$ -ангеликалактона не ухудшает механические свойства сополимеров и придает им способность к биоразложению.

**Ключевые слова:** сополимеризация, стирол,  $\alpha$ -ангеликалактон, биоразложение.

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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

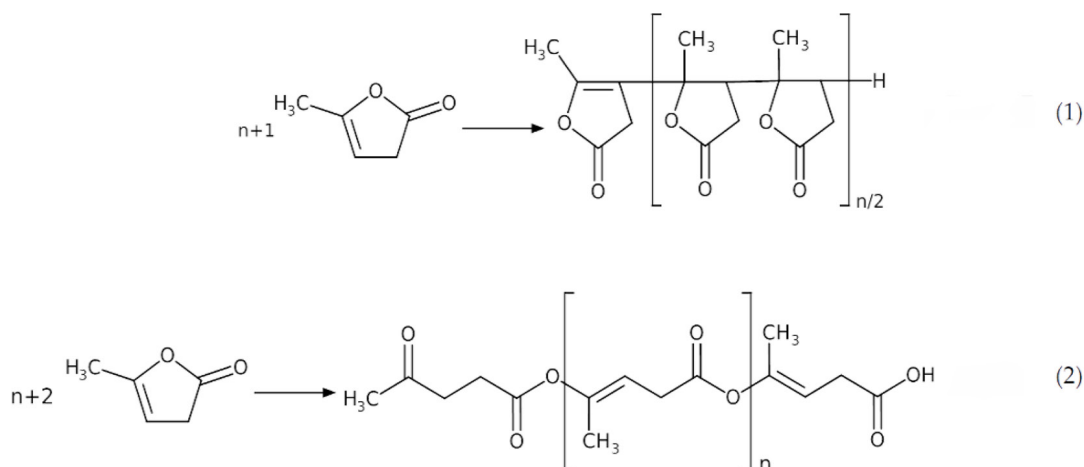


Fig. 1. Possible routes of AL polymerization: (1) polyfuranone formation; (2) polyester formation

copolymers with monomers or polymers that have this ability. One new biodegradable polymer is polyangelicalactone (PAL), a product of the anionic polymerization of  $\alpha$ -angelicalactone (5-methyl-2(3H)-furanon, AL).  $\alpha$ -Angelicalactone (lactone of levulinic acid) is obtained from renewable raw materials, fructose, cellulose, and other carbohydrates [5].

The structure of the AL molecule suggests two possible polymerization routes: opening the double bond to form polyfuranone and opening the lactone cycle to form polyester (Fig. 1) [5–10].

The most interesting reactions are the AL polymerization with opening of the lactone ring (2), which occurs in the presence of sodium hydroxide, sodium butylate [5, 7–9], and stannous octoate ( $\text{Sn}(\text{Oct})_2$ ) [10]. The products of such reactions have the ability to biodegrade [5, 7–9].

Low-molecular PAL samples ( $M_w$  800–1100) undergo almost complete biodegradation via the species *Candida parapsilosis* and *Saccharomyces cerevisiae* within 5–15 days and through *Streptomyces lividans* and *Streptomyces anulatus* within 20–30 days [5, 7]. The polyfuranone ( $M_w$  800–900) obtained by the cationic AL polymerization is not biodegraded by these microorganisms. 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 [7].

Polystyrene (PS) is widely used, for example, to manufacture disposable tableware. This increases the amount of polymeric waste dispersed throughout the environment. The problem of environmental pollution caused by these wastes can be solved by producing biodegradable modifications of polystyrene [12–14].

The copolymerization products of AL and PAL with styrene (St) and other monomers 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. Biodegradable 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 [7]. The emulsion PAL polymerization with St was also carried out. High-impact biodegradable graft-copolymers ( $M_w$  40,000–1,000,000) containing 5–40 wt.% of styrene were prepared [15]. Synthesis and biodegradation of graft-copolymers styrene–polyangelicalactone were studied in [16–17].

The purpose of this work is to study the synthesis, biodegradation, and other properties of polystyrene modified by  $\alpha$ -angelicalactone with a wide range of compositions contained 0–100 % of AL, and to compare the obtained results with the data on graft-copolymers styrene–polyangelicalactone [16–17].

### Materials and methods

Purification of  $\alpha$ -angelicalactone (Alfa Aesar, 98 %), styrene (“Khimreaktivsnab”, “Pure”, 1 % of hydroquinone) and tetrahydrofuran (“Khimreaktivsnab”, “Pure”) are described in [16]. 4,4'-azo-bis-(4-cyanopentanoic) acid was obtained according to [18].

The St and AL radical copolymerization was carried out in the bulk in the presence of 4,4'-azo-bis-(4-cyanopentanoic) acid as the initiator. Calculated amounts of the styrene,  $\alpha$ -angelicalactone, and initiator were placed into the glass ampoule for polymerization. Then the ampoule was vacuumed, filled with argon, and sealed. The sealed ampoule was thermostated at 130 °C. The viscosity of the polymerizing mixture increased during heating, and the temperature of the bath was raised up to 210 °C so that the mass remained viscous.

The removal of unreacted monomers from the resulting copolymers was carried out via extraction in solvents for 8 hours, followed by reprecipitation. The solubility of the copolymers was determined in a sevenfold amount of solvent at room temperature, and the mixture was periodically stirred over 2 hours. In case of partial solubility or swelling of the copolymer, the solubility was assessed at an elevated temperature. The molecular weight was then determined from the intrinsic viscosity measurements using the Ostwald method.

The physical and mechanical characteristics (breaking stress, yield strength, and elongation at break) were determined by the usual methods at a test temperature of  $20 \pm 2$  °C. Water absorption was determined by increasing the weight of the polymer specimens immersed in distilled water for 24 hours at  $21 \pm 2$  °C.

Biodegradation of the copolymers in soil was studied on samples of gray forest soil (Greyic Phaeozems (Albic), WRB, 2006). Samples of soil 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», 260 m a.s.l.). In an area of about 1000 m<sup>2</sup>, twenty samples of soil with a total weight of 10 kg were collected. 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,  $32.4 \pm 2.6$  wt%; pH of water extract,  $5.2 \pm 0.3$ ; humus content, 4.3 wt%; total organic carbon content,  $31.2 \pm 0.2$  mg/g; total nitrogen content,  $2.1 \pm 0.6$  mg/g. Properties of soil was determined by the chemical methods [19].

In a sterile chamber, polymer samples  $5 \times 5 \times 1$  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 described in [17]. The system was thermostated at 24 °C for a duration of 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.

## Results and discussion

### *Physical and chemical properties of polymers*

Fig. 2 shows the dependences of the yield and average molecular weight of the polymerization products of the styrene–angelicalactone (St-AL) and also styrene–polyangelicalactone (St-PAL) [16] mixtures on the components in the reaction mass.

The yield of the resulting copolymers was reduced from 95 % to 70–80 % by increasing the concentration of AL and PAL in the reaction mass from zero to 100 mol%. In the presence of 3–60 % AL, the copolymer yield was 87–89 % and was also practically independent on the AL concentration. These yields were systematically higher than the yields of the PAL graft-copolymer. With AL and PAL concentrations of more than 60 %, there was a gradual decrease in the yield of both graft-copolymer and copolymers to 70–80 %.

The molecular weight of PS obtained by the St radical polymerization under the studied conditions was  $125,000 \pm 8000$ . The molecular weights of copolymers decreased to 2500 by increasing the AL content in the polymers. Graft-copolymers with PAL had higher molecular weights and monotonically decreased to 45,000 with an increase in the PAL content.

The systematic decrease in the molecular weights of copolymers by increasing the content of AL and PAL indicates a break in the polymerization chains of relatively inactive olefin fragments of AL and its polymers. However, the interaction of high-molecular PAL ( $M_w$  15,000–19,000) with St of low concentrations (1–5 %) led to an increase in the molecular weight of the copolymer by an order of magnitude, up to  $M_w$  200,000–500,000 [13]. This means that small styrene additives can initiate the polymerization of PAL with the formation of net structures.

Fig. 3 shows the data on the solubility of the obtained copolymers in various solvents. All the obtained polymers are dissolved in a mixture of DMSO (65 %), DMFA (30 %) and acetic acid (5 %). Only copolymers with the lactone content of  $\geq 95$  mol.% are soluble in acetone.

The solubility of the copolymers increased by increasing the content of AL or PAL in their structures, and AL copolymers were a little better soluble than PAL graft-copolymers. The solubility of the polymers decreased under the following solvents, from most to least effective:

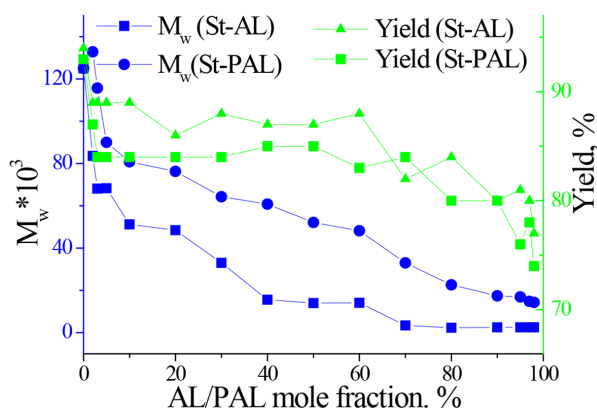


Fig. 2. The influence of the composition of styrene–angelicalactone and styrene–polyangelicalactone mixtures on the yield and average molecular weights of the resulting copolymers. The data on St-PAL graft-copolymers are cited from [16]

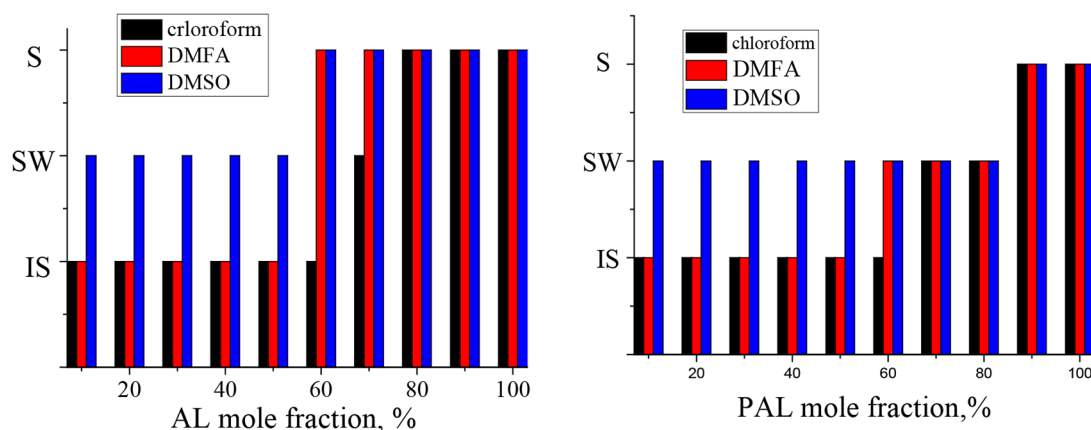


Fig. 3. Solubility of St-AL (left) and St-PAL [16] (right) copolymers (DMFA – dimethylformamide, DMSO – dimethylsulfoxide). IS – insoluble, SW – swells, S – soluble

DMSO > DMFA > chloroform > acetone.

The physical and mechanical characteristics of the studied copolymers and graft-copolymers are presented in Table 1. When passing from PAL, the tensile strength was reduced by half, the yield strength was reduced by one and a half times, and the elongation at break increased by two orders of magnitude. Water absorption of the obtained copolymers increased from 0.4 % to 1.82 % for graft-copolymers of PAL, and from 0.4 % to 1.17 % for copolymers of AL with a decrease in the styrene content.

Thus, an increase in the content of PAL or AL in the initial mixture led to an increase in the flexibility of the macromolecules of the copolymers, which affected the softening temperature and physical and mechanical properties of the synthesized polymers. In addition, the presence of a polyester fragment in the structure of the copolymer cause the formation of adhesive properties. PS had the greatest strength, and PAL provided the best elastic properties. These characteristics for copolymers smoothly changed according to the composition. Notably, under low AL and PAL contents (0–20 %), the decrease in the strength indicators and increase in the water absorption of the copolymers were within 10 %.

Table 1. Physical and mechanical characteristics of the St copolymers and graft-copolymers with AL and PAL [16], respectively

[AL], molar%	Ultimate tensile strength, MPa ( $\pm 4$ )		Elongation at break, % ( $\pm 7$ %)		Yield strength, MPa ( $\pm 4$ )		Water absorption, % ( $\pm 4$ %)	
	AL	PAL	AL	PAL	AL	PAL	AL	PAL
0	38	38	1.23	1.23	29	29	0.4	0.4
20	37	37	12.36	12.5	26	26	0.47	0.48
40	33	33	118.20	120	20	20	0.57	0.58
60	27	28	478.98	490	21	21	0.70	0.72
80	22	23	580.64	608	19	20	1.17	1.23
100	-	21	-	625	-	18	-	1.82

*GC–MS study of copolymerization*

A typical chromatogram of the reaction mass after removing the formed polymer (Fig. 4) revealed the following peaks. In the region from 5 to 9 min, there were signals of monomeric reagents (styrene,  $\alpha$ - and  $\beta$ -angelicalactones) and small quantities of products of St oxidation (benzaldehyde and phenylethylenoxide).

The mass spectrum of the chromatogram peak at 17.7 min ( $(m/z)$ :(intensity): (202:12), (187:5), (157:100), (143:40), (128:30), (115:25), (105:24), (91:26), and (77:18)) was suggested to identify by the database as 5-(2,5-dimethylphenyl)-4-methylfuran-2(5H)-one. However, the database spectrum differs from the experimental one in its intensive signal of  $m/z = 133$  (80 %) and high molecular ion signal intensity (63 %). The proximity of the experimental and the database spectra show that the chromatogram peak in question belongs to the interaction product of a styrene molecule with an AL molecule, possibly 5-methyl-4-(1-phenylethyl)furan-2(3H)-one. This dimer can be formed as a result of terminating a chain starting with styrene and ending with the release of a proton from the furan ring instead of continuing the chain (Fig. 5).

A possible scheme for the destruction of the dimer under mass spectrometry conditions is shown in Fig. 6. An outline of the chain propagation in the copolymerization of  $\alpha$ -angelicalactone and styrene is shown in Fig. 7.

The 18.18 min chromatogram signal was identified in the database as 1,2-diphenylcyclobutane, a product of styrene dimerization. The peak at 26.7 min in the chromatogram was identified as a styrene trimer with a molecular ion ( $m/z = 312$ ; 4 %), a deprotonated dimer and monomer signal ( $m/z = 207$ ; 20 % and 103; 5 %), and an intense signal (100 %) of a benzyl cation. Thus, the GC–MS spectrometric

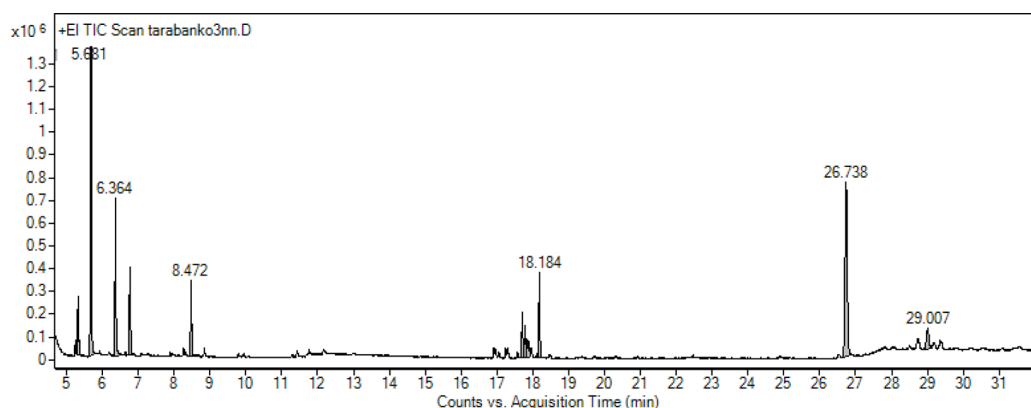


Fig. 4. A typical chromatogram of the reaction mass after removing the copolymers

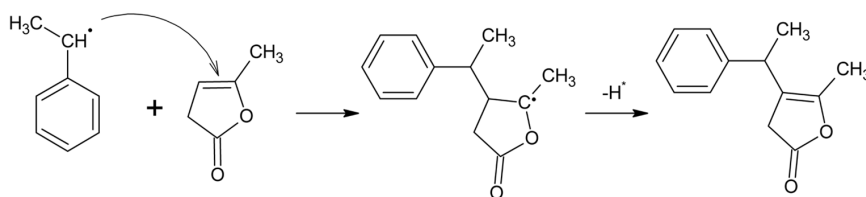


Fig. 5. Possible route of 5-methyl-4-(1-phenylethyl)furan-2(3H)-one formation

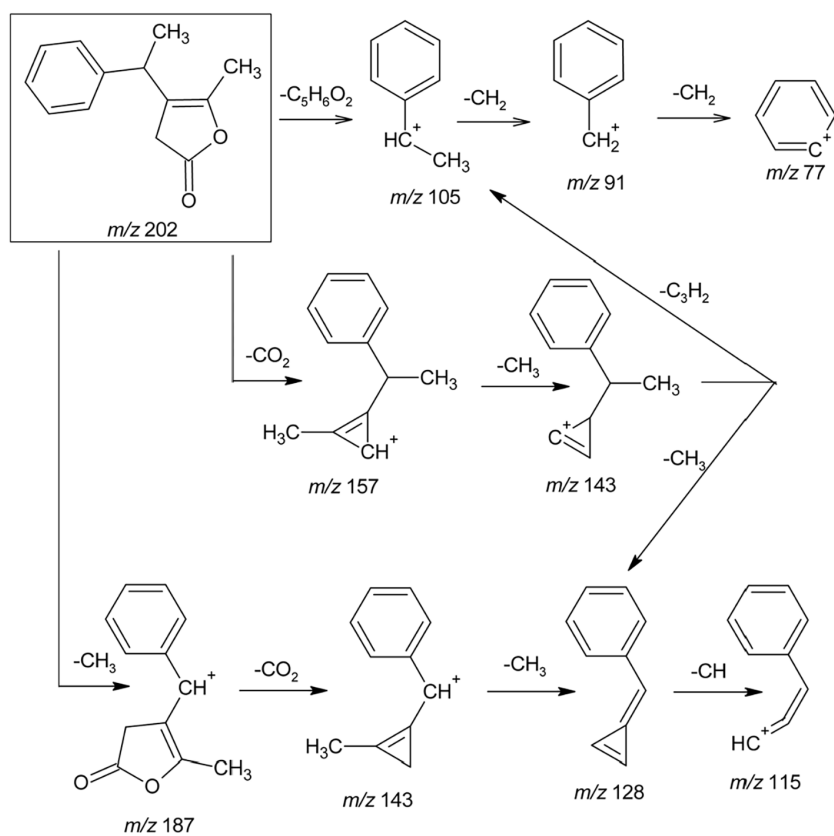


Fig. 6. Possible scheme for the destruction of the dimer under mass spectrometry conditions

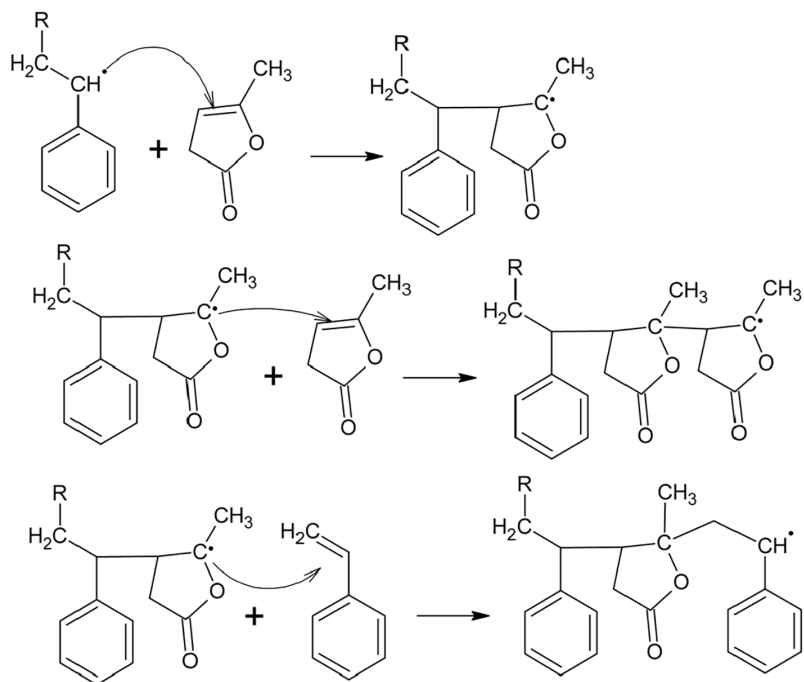


Fig. 7. Scheme of the chain propagation in the copolymerization of St and AL



analysis of the low-molecular products of the copolymerization process indicates the possibility of product formation under St and AL interactions.

#### *Biodegradation of the obtained copolymers in the soil*

Fig. 8 shows the results of the biodegradation of St-AL and St-PAL copolymers [17] in the gray soil. All the copolymer samples, starting from 2 wt.% of AL or PAL content, were completely destroyed in 28 weeks. After this period, none of the copolymer particles were observed in the soil.

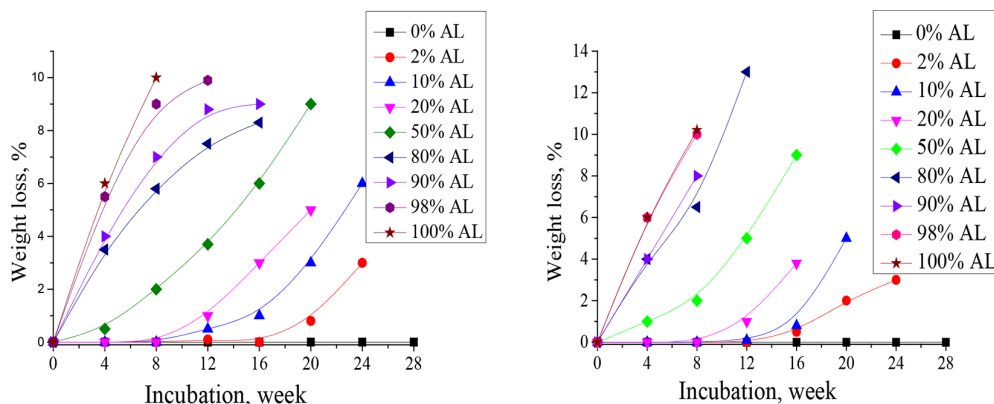


Fig. 8. Weight loss of AL–St (left Fig.) and PAL–St (right Fig. [17]) samples during incubation in soil. The last point in the curves means that during next month a complete mechanical destruction of the samples occurs

In general, the St-AL copolymers were more stable than the St-PAL graft-copolymers under the conditions of biodegradation, and the latter degraded mechanically four weeks earlier than the former. This difference may be caused by the significant content of ester bonds in the PAL obtained via anionic polymerization, with fewer of these bonds observed in the St-AL copolymers obtained via radical polymerization (see Scheme 1, Equations (1) and (2)).

The first stage of graft-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 ( $\geq 50$  wt%) occurred after weight loss of approximately 10 %. The copolymers with a low content of AL ( $\leq 30$  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. This induction period may be connected with accumulation of microorganisms being possible to assimilate the AL structures of the copolymers.

The results of microbiological analysis of destructed samples of St-PAL graft-copolymers, the species composition of micromycetes, as well as data confirming the absence of toxicity of aqueous extracts of copolymer biodegradation products are presented in [17]. It can be assumed that the process of biodegradation of St-AL copolymers considered in this paper proceeds similarly, giving non-toxic degradation products.

## Conclusions

Series of polymeric compositions of styrene and  $\alpha$ -angelicalactone was obtained via the method of radical copolymerization. The dimeric product of the interaction of AL and St molecules was registered among the products of radical polymerization by GC–MS.

Increasing the portion of St units in the copolymers improved the strength properties and increased fragility. Increasing the AL or PAL content in the polymeric compositions increased the elasticity of the materials obtained. The obtained copolymers have physical and mechanical properties corresponding to the requirements for plain polystyrene.

In the process of incubating the copolymers 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 were mechanically destroyed within 28 weeks. The most unexpected result of this study is the close rates of biodegradation of the copolymers with the polyfuranone and polyester structures formed as a result of  $\alpha$ -angelicalactone polymerization with styrene. Copolymer compositions with AL content up to 20 % are most suitable for many uses.

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<sub>2</sub> and H<sub>2</sub>O. The obtained results show that the modification of polystyrene with impurities of PAL or AL can at least solve the first problem without worsening the properties of the copolymers.

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