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Synthesis and Properties of Polymers Based on Styrene and α -angelicalactone

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Abstract. Polyangelicalactone-*graft*-polystyrene copolymers were obtained through cationic polymerization. Increasing the portion of styrene units in the copolymers improves the strength properties and increases fragility. Increasing the polyangelicalactone(PAL) content in the copolymers increases the elasticity of the materials obtained. The obtained copolymers are greatly a composition of PAL and polystyrene (PS) with a small content of bonds of styrene-units of 4-alkoxypent-3-enoic acid. Low α -angelicalactone(AL) content in styrene copolymers improves the oxidative stability of the copolymers. The resulting PAL-*graft*-PS copolymers have physical and mechanical properties corresponding to the requirements for general-purpose PS.

Keywords: 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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Синтез и свойства полимеров на основе стирола и α -ангеликалактона

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Аннотация. Методом катионной полимеризации получены сополимеры полиангеликалактона(PAL) с привитым полистиролом (PS). Увеличение доли стирольных звеньев улучшило прочностные свойства и повысило хрупкость сополимеров, а увеличение содержания PAL повысило их эластичность. Полученные материалы представляют собой композицию PAL и PS с небольшим содержанием связей стирол-звено 4-алкоксипент-3-еновой кислоты и обладают физико-механическими свойствами, соответствующими требованиям, предъявляемым к полистиролу общего назначения. Небольшое содержание α -ангеликалактона в сополимерах стирола улучшает их окислительную стабильность.

Ключевые слова: 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). AL (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 ($\text{Sn}(\text{Oct})_2$) [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 [10,11].

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].

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 biodegradable modifications of polystyrene[12–15].

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 emulsion polymerization of PAL 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 [16].

The goal of this work is to study the synthesis and properties of polyangelicalactone-*graft*-polystyrene (PAL-*graft*-PS) with a wide range of compositions.

Experimental part

AL (Alfa Aesar, 98 %) was purified before use via fractional melt crystallization. The styrene («Khimreaktivsnab», «Pure», 1 % of hydroquinone) was washed sequentially once with an aqueous solution of NaOH (5 wt%) and four times with water, dried over anhydrous sodium sulfate, and then

distilled in a vacuum. The aluminiumisopropoxide was obtained according to the method in [17]. Tetrahydrofuran (THF) («Khimreaktivsnab», «Pure») was washed with a saturated aqueous solution of NaOH, distilled in a vacuum, purified by prolonged reflux in the presence of sodium metal with the addition of benzophenone (0,2–0,3 wt%) under the flow of purified argon, and then distilled in a vacuum. Methylene chloride was refluxed in presence of sodium metal, and then distilled in a vacuum. Boron trifluoride etherate (BF_3OEt_2) was distilled under reduced pressure. Other chemicals were used as received.

PAL was obtained via ring opening polymerization in a solution in tetrahydrofuran in the presence of aluminiumisopropoxide and benzophenoneketyl-Na. In total, 100 mL of carefully dried tetrahydrofuran, 0,06 g of benzophenone, and 0,01 g of metallic sodium (small scales) were placed in a 0,25 L flask with a reflux condenser. After the formation of benzophenoneketyl-Na, 0,6 g of aluminiumisopropoxide was loaded into a flask under an argon flow. Then, 10 g of AL was loaded into the system. The duration of polymerization was 60 minutes at reflux. After cooling obtained polymer was precipitated by ethanol and washed decantation with several portions of cold diethyl ether, and freed of volatile matter by heating at 80 °C and 2 Torr during one and half hours. There remained 7,6 g of a slightly yellow solid. THF/ethanol system was used to fractionation of products. For this study, PAL with $M_w \sim 6000 \text{ g} \times \text{mol}^{-1}$ was used.

Cationic styrene (St) polymerization, and polyangelicalactone grafting with styrene was performed in the presence of boron trifluoride etherate as the catalyst. The boron trifluoride etherate as well the solution of the calculated amounts of the styrene and polyangelicalactone in methylene chloride were thermostated at $-16 - -18 \text{ }^\circ\text{C}$ for 30 minutes before mixing. The monomers solution was placed into the glass tube, and then $\text{BF}_3 \cdot \text{OEt}_2$ was added. After a predetermined time, ice-cold ethanol was added, and then volatile products were evaporated. The removal of unreacted monomers from the precipitated crude product was carried out via extraction in ethanol for 8 hours, followed by dissolution and reprecipitation in the THF/ethanol system.

The molecular weights were defined using the gel permeation chromatography (GPC) method. For chromatographic measurements, the samples were dissolved in the mobile phase ($\sim 5 \text{ mg/ml}$) and filtered through a $0,22 \text{ } \mu\text{m}$ PTFE membrane filter. The GPC measurements were made using an Agilent 1260 Infinity II Multi-Detector GPC/SEC System chromatograph with triple detection: by a refractometer, by a viscometer and by a light scattering. Separation were made on PIGel Mixed-E and PIGel Mixed-B columns using THF stabilized by 250 ppm BHT as the mobile phase, the flow rate of the eluent was 1 ml/min. All columns were calibrated using polydisperse polystyrene standards (Agilent, USA).

The breaking stress, yield strength, and elongation at break were determined using the tensile machine ZMGi-250 by the standard plastics tensile test methods at a test temperature of $20 \pm 2 \text{ }^\circ\text{C}$. The brittleness temperatures were determined using the device for measuring the brittleness of plastics PHP-3. Water absorption was determined by increasing the weight of the polymer specimens immersed in distilled water for 24 hours at $21 \pm 2 \text{ }^\circ\text{C}$.

The ^1H NMR spectra were measured using a BrukerAvance III 600 spectrometer at 300 K.

Thermogravimetric analysis was carried in a corundum crucible using an STA 449 F1 Jupiter instrument (NETZSCH) in a temperature range from 30 to 800 °C in an argon/air flow (the flow rates of shielding and purge gases were 20 and 50 mL/min, respectively).

Results and discussion

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

Samples were prepared by changing the molar ratio of PAL to St, maintaining the molar ratio $\text{BF}_3\cdot\text{OEt}_2/\text{St} = 0,02$, as shown in Table 1.

The yield of the resulting copolymers was reduced from 87 % to 74 % by increasing the concentration of PAL in the reaction mass from 2 to 98 mol%. The molecular weight of polystyrene obtained under the studied conditions was 125,000. The molecular weights of copolymers decreased to 14300 by increasing the PAL content in the polymers.

The systematic decrease in the molecular weights of copolymers by increasing the content of PAL indicates a break in the polymerization chains of relatively inactive olefin fragments of PAL.

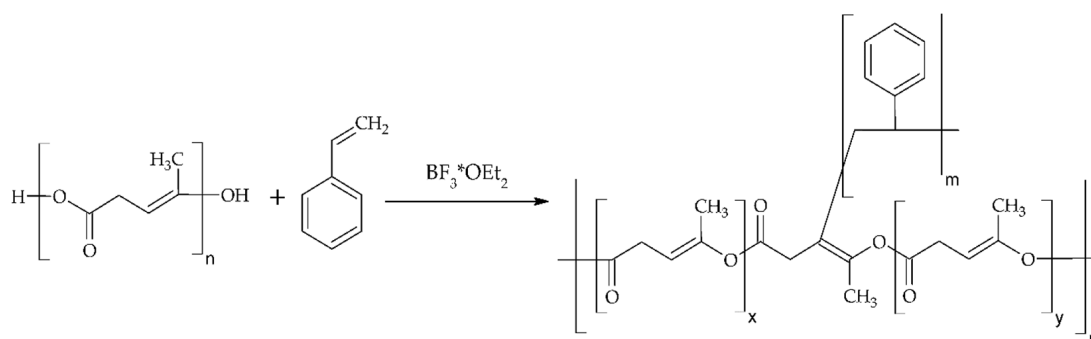


Fig. 1. Scheme of polystyrene grafting of polyangelicalactone

Table 1. The influence of the composition of PAL and St mixtures on the yield, molar masses and polydispersities of the resulting PAL-g-PS copolymers

Sample	PAL, mmol	St, mmol	Polymer yield, wt%	M_w ($\pm 6\%$), g mol^{-1}	PDI (M_w/M_n)
PAL-g-PS [2:98]	2	98	87	132800	2,19
PAL-g-PS [3:97]	3	97	84	115700	2,45
PAL-g-PS [5:95]	5	95	84	90000	1,98
PAL-g-PS [10:90]	10	90	84	80800	1,96
PAL-g-PS [20:80]	20	80	84	76300	2,00
PAL-g-PS [30:70]	30	70	84	64300	2,04
PAL-g-PS [40:60]	40	60	86	60800	2,02
PAL-g-PS [50:50]	50	50	86	52100	2,19
PAL-g-PS [60:40]	60	40	83	48200	2,32
PAL-g-PS [70:30]	70	30	84	33000	2,34
PAL-g-PS [80:20]	80	20	80	22600	2,27
PAL-g-PS [90:10]	90	10	80	17400	2,15
PAL-g-PS [95:5]	95	5	76	16900	2,16
PAL-g-PS [97:3]	97	3	78	14800	2,00
PAL-g-PS [98:2]	98	2	74	14300	2,12

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 [6]. This means that small styrene additives can initiate the grafting of PAL with the formation of net structures.

NMR study of polymers

The formation of the synthesized PAL, PS and PAL-g-PS was confirmed by ^1H NMR spectroscopy. Figure 2 shows the ^1H NMR spectra of the PAL, PS and the PAL-g-PS [40:60] copolymer.

Comparing three spectra shows, that the copolymer spectrum is mainly superposition of homopolymers spectra (a) and (b). This means that the copolymer obtained is greatly a composition of PAL and PS.

Nevertheless, the spectra of products of water–alkaline hydrolysis of the copolymers contained mostly signals of levulinic acid as well as small peaks of protons of the phenyl group (about 1 %). We assume that the styrene fragments passed into the aqueous phase in the form of water-soluble hydrophilic compounds as a result of copolymerization with double bonds of the ester units of 4-alkoxypent-3-enoic acid.

Physical and chemical properties of polymers

The physical and mechanical characteristics of the studied copolymers are presented in Table 2. When passing from polystyrene to polyangelicalactone, 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

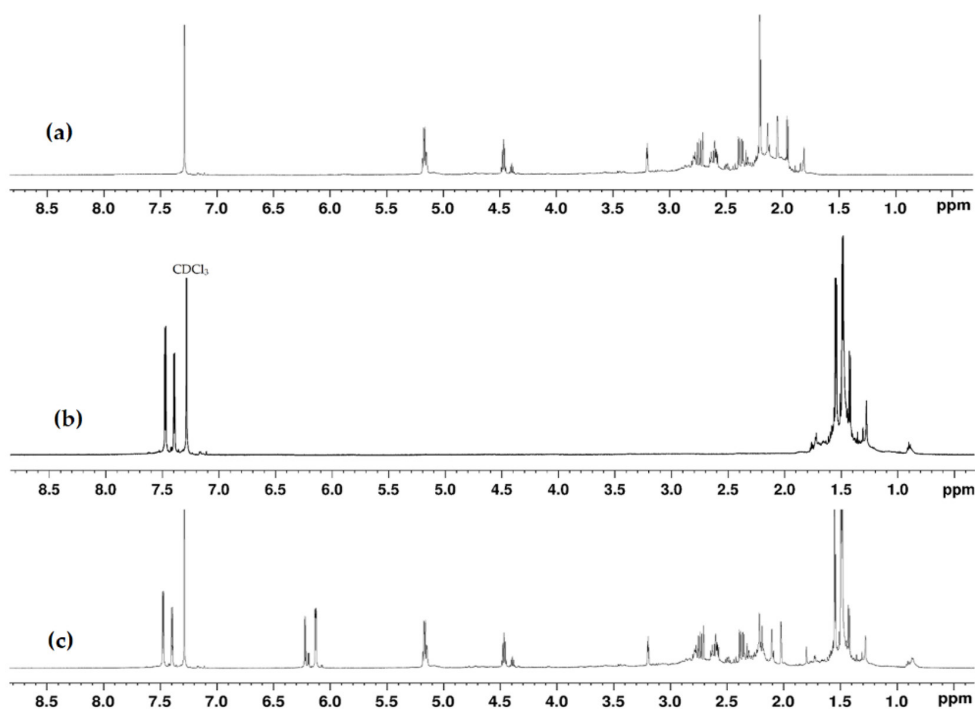


Fig. 2. ^1H NMR spectra of the PAL (a), PS (b) and the PAL-g-PS [40:60] (c) copolymer

Table 2. Physical and mechanical characteristics of obtained PS, PAL-g-PS, and PAL polymers

Sample	Ultimate tensile strength, MPa (± 4)	Elongation at break, % (± 7 %)	Yield strength, MPa (± 4)	Water absorption, % (± 4 %)
PS	38	1,23	29	0,4
PAL-g-PS [20:80]	37	12,5	26	0,48
PAL-g-PS [40:60]	33	120	20	0,58
PAL-g-PS [60:40]	28	490	21	0,72
PAL-g-PS [80:20]	23	608	20	1,23
PAL	21	625	18	1,82

orders of magnitude. Water absorption of the obtained copolymers increased from 0.4 % to 1.82 % for copolymers of PAL with a decrease in the styrene content. The brittleness temperature of the resulting polymers was in the range of -38 to -48 °C and increased by increasing the content of PAL in the copolymers.

Thus, an increase in the content of PAL 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 causes the formation of adhesive properties. Polystyrene had the greatest strength, and PAL provided the best elastic properties. These characteristics for copolymers smoothly changed according to the composition. Notably, under low PAL contents (0 %–20 %), the decrease in the strength indicators and increase in the water absorption of the copolymers were less than 10 %.

Thermochemical study of polymers

The results for the differential thermogravimetical analysis of the obtained polymers are presented in Fig. 3.

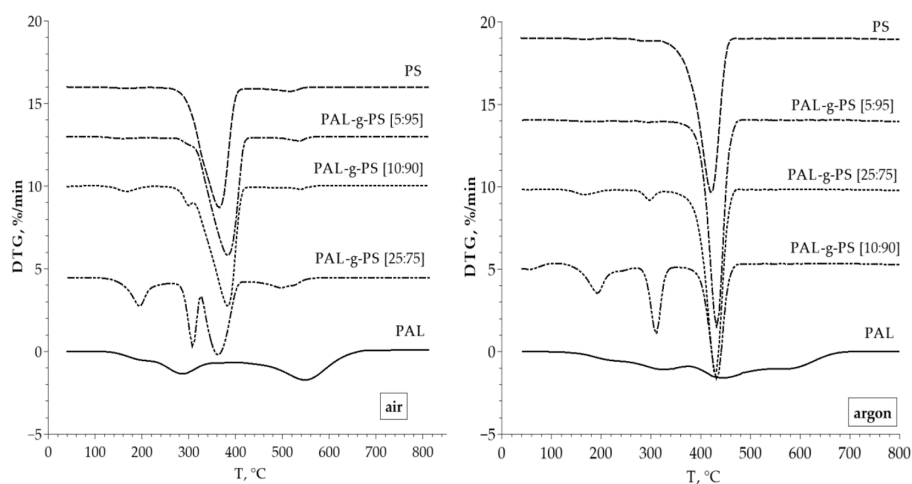


Fig. 3. Differential thermogravimetical curves of the PAL-g-PS copolymers

In an argon atmosphere, pure polystyrene began to decompose, with weight loss observed at 300 °C and the maximum decomposition rate occurring at 409 °C. Styrene and AL copolymers exhibited two additional maximum mass loss rates at 220 and 295 °C.

In the air atmosphere, the maximum weight loss rate of the pure polystyrene sample was shifted by 55 degrees to the low temperature range down to 354 °C, and the temperature of this maximum was practically independent of the PAL content in the copolymer. The position of the maximum at 295 °C was practically independent of both the PAL content and the composition of the gas phase. The latter indicates oxidative processes with a loss of polymer mass beginning at higher temperatures. These results show that small additions of polyangelicalactone to polystyrene can improve the oxidative stability of the copolymer without changing its heat resistance.

Conclusions

Series of polyangelicalactone-*graft*-polystyrene copolymers were obtained through cationic polymerization. Increasing the portion of St 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.

The ¹H NMR study shows that the copolymer spectrum is mainly superposition of the homopolymer corresponding spectra. This means that the copolymer obtained is greatly a composition of PAL and PS. Nevertheless, the spectra of products of water–alkaline hydrolysis of the copolymers contained mostly signals of levulinic acid as well as small peaks of protons of the phenyl group (about 1 %). We assume that the styrene fragments passed into the aqueous phase in the form of water-soluble hydrophilic compounds as a result of copolymerization with double bonds of the ester units of 4-alkoxypent-3-enoic acid.

According to the thermogravimetric data, styrene copolymers with low AL content up to 5 % did not practically lose their thermal resistance in the inert atmosphere compared to the homopolymer. Moreover, small additions of angelicalactone to polystyrene improved the oxidative stability of the copolymers.

Thus, the resulting polyangelicalactone-*graft*-polystyrene copolymers have physical and mechanical properties corresponding to the requirements for general-purpose polystyrene. Probably, the copolymers are biodegradable, and a corresponding study is in progress.

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