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Synthesis of Copolymers of Furandicarboxylic Acid, Ethylene Glycol, and Poly(Angelica Lactone)

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This work demonstrates the possibility of creating biodegradable derivatives of poly(ethylene furandicarboxylate) by modification with poly(angelica lactone) chains. Block copolymers with the content of angelica lactone 33-50 mol. % (based on monomeric links) were obtained. Polymer yields were 60-70 %, and weight average molecular weights attained 36-45 kDa. The results of the polymers biodegradation are presented.

Keywords: copolymers, furandicarboxylic acid, ethylene glycol, poly(angelica lactone), biodegradable polymers.

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Получение сополимеров фурандикарбоновой кислоты, этиленгликоля и полиангеликалактона

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Продемонстрированы возможности создания биodeградируемых модификаций полиэтиленфурандикарбоксилата путем его модификации цепями полиангеликалактона. Получены блок-сополимеры с содержанием мономерных звеньев ангеликалактона в цепи полимера 33-50 мол. %. Выходы полимеров составляют 60-70 %, их средневесовые молекулярные массы достигают 36-45 тыс. а.е.м. Представлены результаты биodeградации полученных полимеров.

Ключевые слова: сополимеры, фурандикарбоновая кислота, этиленгликоль, полиангеликалактон, биodeградируемые полимеры.

Introduction

Wide distribution of polymeric materials in various fields of industry and market leads to the increasing amount of waste polymers, some of which find no disposal. For this reason, imparting polymers with the ability to decompose into safe nontoxic compounds in the environment is a relevant problem. One of the ways to make a polymer biodegradable is to produce its copolymers with monomers or polymer blocks that are biodegradable themselves [1-3]. For example, renewable-feedstock-derived α -angelica lactone (2,3-dihydro-5-methylfuran-2-one) and its anionic polymerization product poly(angelica lactone)—itself a biodegradable unsaturated polyester [4]—are capable of co-polymerizing with polyesters, polyolefins, and caprolactam [5].

The molecular structure of α -angelica lactone dictates two possible polymerization pathways (Fig. 1): the double bond opening that leads to the polyfuranone (1), and the ring opening that leads to the polyester (2).

Polyfuranone formation takes place in the presence of strong Lewis acids, or under ionizing radiation [6]. This produces oligomers with $n = 5-8$ and melting point 257-259 K.

However, α -angelica lactone polymerization via ring opening is of greater interest. This reaction proceeds in the presence of sodium hydroxide, sodium butoxide [4], stannous octanoate [7]. The products of this reaction are capable of biodegradation [5].

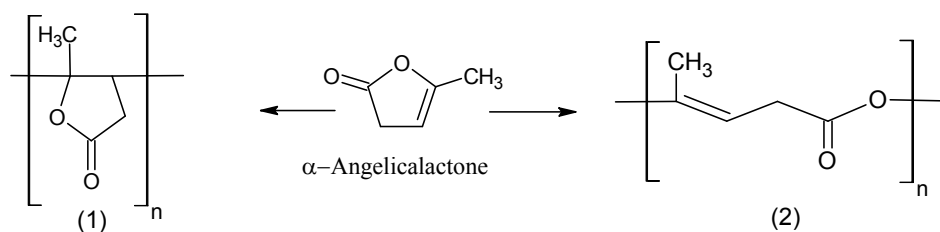


Fig. 1. Possible α -angelica lactone polymerization pathways

The α -angelica lactone polyester modified during polymerization with styrene has physicomechanical properties similar to those of general-purpose polystyrene, and can biodegrade in grey forest soil (Haplic Greyzem) [8].

Furan-2,5-dicarboxylic acid (FDCA) is a promising potentially versatile product obtained by oxidation of 5-hydroxymethylfurfural, itself a product of acid-catalyzed hexose carbohydrate conversion. FDCA is considered as a renewable feedstock for production of poly(ethylene furandicarboxylate)–PEFDC—a polymer analogous to polyethylene terephthalate [9].

Polyethylene furandicarboxylates are quite resistant to biodegradation. However, FDCA-based polyesters are generally expected to be biodegradable [10-13]. Polymers structurally equivalent to PEFDC made with butandiol-1,4, as well as copolymers with adipic acid are more prone to biologically decompose [10]. Although if the FDCA portion of the acid component in a copolymer poly(butylene adipate – co – butylene furandicarboxylate) is 75-100 mol. %, then this polymer becomes impervious to destruction by porcine pancreatic lipase [10].

The goal of the present work is synthesis and comparison of properties (including biodegradability) of poly(ethylene furandicarboxylate) and its copolymers with poly(angelica lactone).

Experimental

α -angelica lactone (98 %, Alfa Aesar), hereinafter α AL, prior to use was distilled under vacuum ($P = 12$ Torr, $T = 328$ K) with consequent fractional melt crystallization.

Furan-2,5-dicarboxylic acid was synthesized according to a method described elsewhere [14].

Poly(α -angelica lactone), hereinafter PAL, was synthesized by anionic polymerization of α AL in the presence of sodium butoxide according to a method described earlier [4].

Molar masses and polydispersity $n = M_w/M_n$ of the obtained polymerization products were estimated by viscometry (Ostwald viscometers, capillary diameters 0.12 and 0.56 mm, solvent–mixture of trifluoroacetic acid and 1,2-dichloroethane, 2:1 by volume) and cryoscopy (in benzophenone).

NMR spectra were recorded with a Bruker AVANCE III 600 (Centre for Collective Use, Federal Research Center “Krasnoyarsk Science Center SB RAS”) at 600 MHz operating frequency.

Synthesis of bis(2-hydroxyethyl) furan-2,5-dicarboxylate. A 250 ml Erlenmeyer flask was loaded with ethylene glycol (100 ml), FDCA (5.165 g, 33.1 mmol), and hydrochloric acid (12 ml of 30.4 % solution, 120 mmol). This produced a brown-colored solution.

This solution was kept at 90 °C for 12 hours, while agitated with a magnetic stirrer. Afterwards, the solution was neutralized by sodium hydroxide (saturated solution in ethylene glycol). The excess of ethylene glycol was removed from the system by evaporation under vacuum.

The result was a viscous deeply colored liquid that did not crystallize at room temperature. This substance was dissolved in acetone at room temperature, impurities were filtered out, and the solvent was removed by evaporation under vacuum.

White crystalline solid was isolated. Yield 70.8 %, m.p. \approx 89-93 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.22 (s, 2H); 4.32 (t, $J = 5.6$ Hz, 4H); 3.87 (t, $J = 5.6$ Hz, 4H); 3.08 (s, 2H).

Catalyst preparation. Air-dried powdered silicate material MCM-41 was immersed in 0.4 N nitric acid solution under intense stirring for 40 minutes. Afterwards, it was filtered and rinsed until the filtrate pH neutrality was attained. The material was then dried at $T = 353$ K until constant mass was reached.

Synthesis of diethyl furan-2,5-dicarboxylate. Stainless steel autoclave (12Kh18N10T steel, analogous to AISI 321) was loaded with anhydrous ethanol (200 ml), FDCA (3.12 g, 20 mmol), and freshly prepared MCM-41 catalyst (4 g). After sealing the autoclave, it was flushed with argon to create inert reaction environment. The autoclave was then heated to 150 °C and kept like that for 6 hours, all with constant agitation with a magnetic stirrer (≈ 900 min^{-1}). Afterwards, once the autoclave cooled down, the reaction mass was filtered and evaporated in a rotary evaporator.

Thus, 2.92 g of yellowish viscous liquid was isolated. It was distilled under vacuum. The principal component is diethyl furan-2,5-dicarboxylate, b.p. 170 °C (at 12 Torr). ^1H NMR (600 MHz, CDCl_3): δ 7.17 (s, 2H), 4.38 (q, $J = 6.9$ Hz, 4H), 1.39 (t, $J = 6.7$ Hz, 6H). Yield 61 %, 2.58 g isolated.

Polymerization of bis(2-hydroxyethyl) furan-2,5-dicarboxylate [15]. A 50 ml round-bottom flask was loaded with thoroughly ground mixture of bis(2-hydroxyethyl) furan-2,5-dicarboxylate (6.50 g, 26.6 mmol) and antimony (III) oxide (65 mg, 0.223 mmol).

The mixture was processed under vacuum (≈ 2 Torr) with a magnetic stirrer agitation. First it was heated to 70 °C, then heated stepwise to 260 °C (step size 10 °C, rest at each step 5-10 min), and kept at the final temperature for 30 min. Afterwards, the system was allowed to cool down to room temperature, keeping it under vacuum in the process.

Pale yellowish-orange solid was obtained.

This product was dissolved in trifluoroacetic acid, precipitated by adding the excess of ethanol, filtered, and the product was dried under vacuum at 60 °C.

Pale yellowish plastic was isolated. Yield 71.5 %, 3.81 g.

Copolymer synthesis. A 50 ml round-bottom flask was loaded with diethyl furan-2,5-dicarboxylate (1.1 g, 5 mmol), powdered PAL (amount corresponding to a desired PAL/FDCA ratio, $M_w \approx 1200$), ethylene glycol (10 ml), and antimony (III) oxide (65 mg, 0.223 mmol).

The mixture was processed under argon atmosphere, with agitation with a magnetic stirrer. It was heated stepwise to 120 °C (step size 10 °C, rest at each step 5 min). Then, the system was evacuated to 2 Torr residual pressure, heated to 240 °C, and kept this way for 30 min. Afterwards, the system was allowed to cool down to room temperature, keeping it under vacuum in the process.

Pale yellowish-orange solid was obtained.

This product was dissolved in trifluoroacetic acid, the catalyst was filtered out, and the product was dried under vacuum at 60 °C.

Pale yellowish plastic was isolated.

^1H NMR (600 MHz, CF_3COOH): δ 2.17, 3.28, 3.85, 4.34, 4.50, 4.77, 6.04, 7.13, 7.21, 7.35.

Biodegradation capability study. Biodegradability of the obtained polymers was estimated under composting conditions. A sample sized 20x20x3 mm inside a stainless steel mesh casing was buried inside a compost heap comprising wetted minced plant matter, impregnated with an organo-mineral fertilizer solution also containing live culture of *Bacillus subtilis* strain 26D. Biodegradation extent was estimated by measuring the sample mass change. To do so, exhumed samples were washed with water, dried, and weighed. Afterwards, the samples were placed back into the compost for continued decomposition.

Results and discussion

Synthesis of poly(ethylene furan-2,5-dicarboxylate) (PEFDC). The polymer obtained by the polycondensation of bis(2-hydroxyethyl) furan-2,5-dicarboxylate has molecular mass $M_w \approx 34000$, which is close to earlier described products ($M_w \approx 44500$ [15]). The polyester ^1H NMR spectrum includes two principal signals: furan ring protons (7.25-7.50 ppm), and alkyl protons of the ethylene glycol fragments (4.5-4.8 ppm).

Synthesis of copolymers of FDCA, PAL, and ethylene glycol. Attempts at co-polycondensation of bis(2-hydroxyethyl) furan-2,5-dicarboxylate poly(α -angelica lactone) according to the aforementioned method [15] did not produce copolymers. On the other hand, experiments demonstrate that co-polycondensation of diethyl furan-2,5-dicarboxylate, PAL, and ethylene glycol is possible (Fig. 2).

Table 1 represents the results of synthesizing block copolymers of PAL, FDCA, and ethylene glycol. The angelica lactone fraction in the block copolymers is 33-50 mol. % (based on monomeric angelica lactone links, the rest being monomeric ethylene dicarboxylate links). The yield of polymers attains 60-70 %, their weight-average molecular weights attain 36-45 kDa.

Figure 3 demonstrates the ^1H NMR spectrum of a synthesized block copolymer. It includes signals from the furan ring protons (6.8-7.7 ppm), protons of ethylene glycol alkyl fragments (4.7-6.0

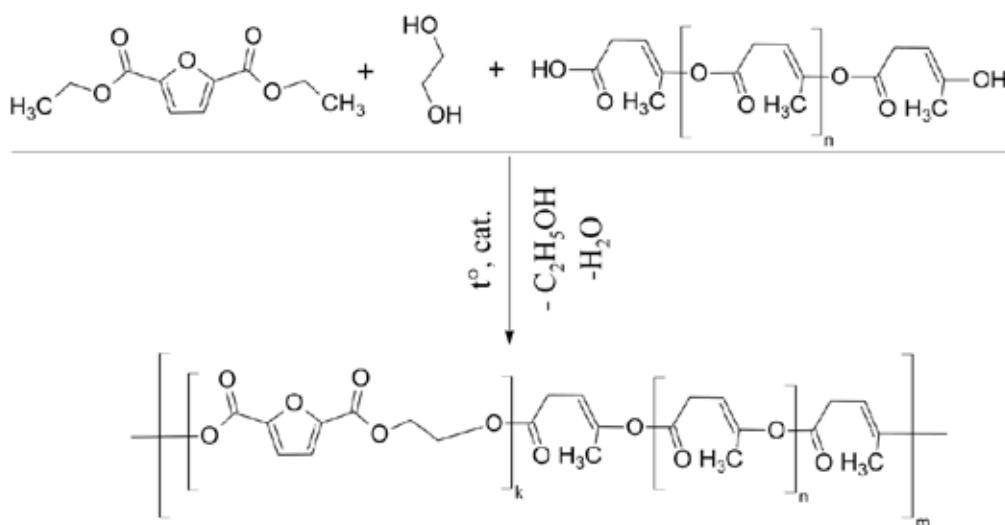


Fig. 2. Co-polymerization of diethyl furan-2,5-dicarboxylate, poly(α -angelica lactone), and ethylene glycol

Table 1. PAL and PEFDC block copolymer synthesis results.

Polymer composition*	Reactant loading			Yield, % of theoretical	M _w **
	Diethyl furandicarboxylate, mol	Ethylene glycol, mol	PAL, mol (based on monomeric links)		
1:1:1	0.005	0.005	0.005	70	41300
4:4:3	0.005	0.005	0.0039	62	36600
2:2:1	0.005	0.005	0.0025	67	44700

* – molar ratio of FDCA : ethylene glycol : aAL in the reaction feedstock (based on monomeric links)

** – weight-average molecular weight of the polymers, viscometric determination

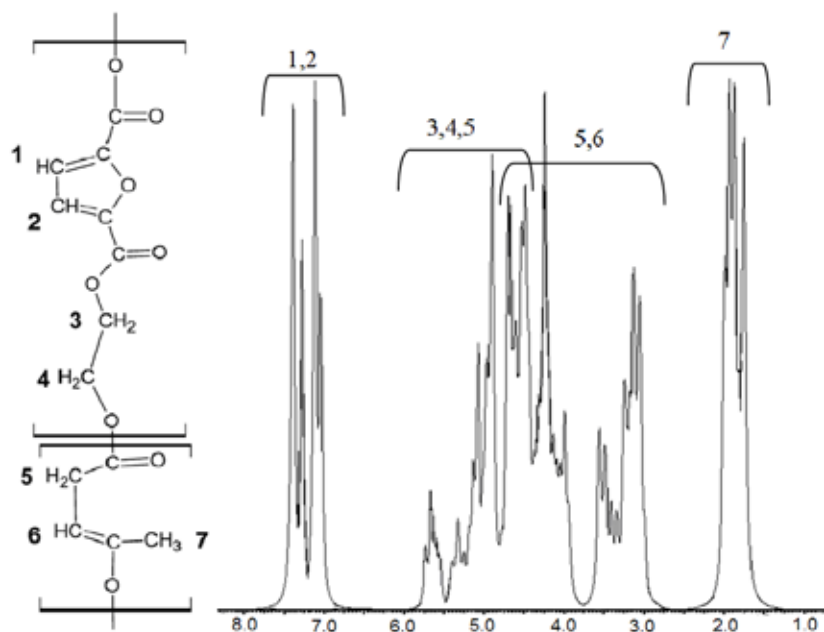


Fig. 3. ¹H NMR spectrum of an obtained block copolymer. The structure to the left is labeled with possible attributions of the NMR signals

ppm), and the protons of the opened angelica lactone rings: methylene and vinyl (2.7-4.7 ppm), and methyl (1.4-2.3 ppm).

Biodegradation of FDCA-based polymers. Figure 4 presents the results of the synthesized polymers biodegradation. Block copolymers with angelica lactone lose 70-80 % of their mass after composting for 40-50 days.

Biodegradation rate is practically independent of the PAL content in the aAL:FDCA ratio range from 1:1 to 1:2. PEFDC that contains no poly(angelica lactone) blocks does not appreciably decompose under the studied conditions. This is consistent with earlier described stability of this polymer against biodegradation [10]. Poly(ethylene terephthalate) is also quite stable under these conditions, while its modification with small amounts of aAL and PAL results in polymers that lose 20-30 % of their mass in similar destruction tests [5].

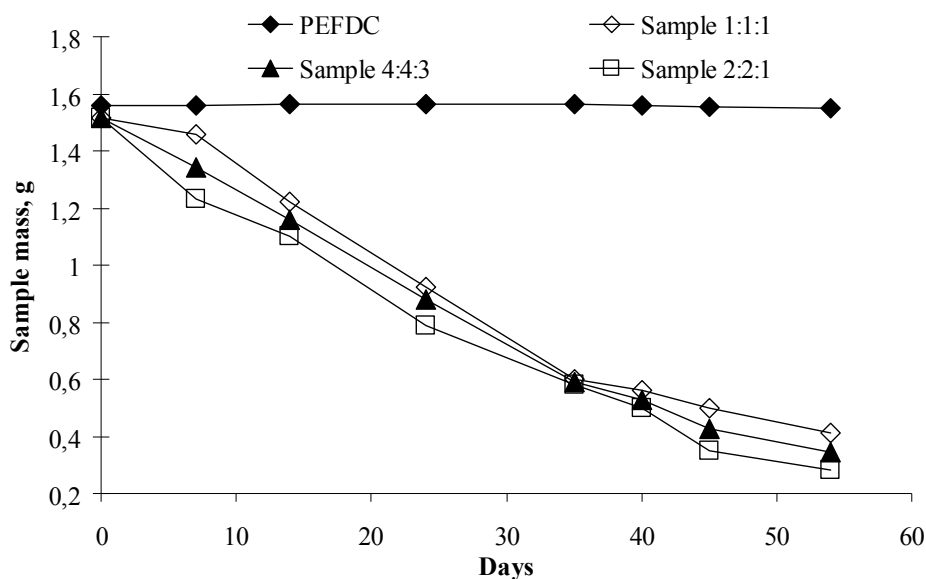


Fig. 4. Mass change of samples of poly(ethylene furan-2,5-dicarboxylate) and its copolymers in biodegradation tests by composting. Co-polymer indices represent their composition (molar ratio of FDCA : ethylene glycol : PAL in the reaction feedstock, based on monomeric links)

It can be concluded that the obtained results demonstrate the possibility of creating biodegradable derivatives of poly(ethylene furan-2,5-dicarboxylate) by modification with poly(α -angelica lactone) chains.

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