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ДИЦИНАМИЛОВЫЙ ЭФИР 2,5-ФУРАНДИКАРБОНОВОЙ КИСЛОТЫ И НОВЫЕ СОПОЛИМЕРЫ НА ЕГО ОСНОВЕ

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Разработан способ синтеза дицинамилового эфира 2,5-фурандикарбоновой кислоты (DCF) – нового непредельного соединения фуранового ряда, потенциального мономера для получения сополимеров с различными виниловыми соединениями и на их основе конструкционных и ионообменных материалов нового поколения. Исследованы реакции радикальной гомополимеризации DCF и его сополимеризации с различными мономерами. DCF не вступает в реакцию гомополимеризации ни в массе, ни в растворе (растворитель: толуол) и самостоятельных полимеров не образует. Однако DCF активно сополимеризуется со стиролом, метилметакрилатом, метакриловой и акриловой кислотами с образованием сетчатых полимеров с различной степенью сшивки. Определены константы сополимеризации DCF с ненасыщенными кислотами, стиролом и метилметакрилатом. Сополимеры DCF обогащены сомономерными звеньями для всех соотношений компонентов исходной реакционной смеси, являются статистическими, и сомономерные звенья в макромолекуле расположены случайным образом. Сополимеры со стиролом или метилметакрилатом имеют более высокую механическую прочность по сравнению с полистиролом и полиметилметакрилатом. Сополимеры, содержащие карбоксильные группы и 10-20% мас. сшивающего агента, проявляют хорошие ионно-обменные свойства по отношению к тяжелым металлам. Равновесная адсорбционная емкость сополимеров DCF с акриловой или метакриловой кислотами по отношению к ионам Cu^{2+} (221 и 234 мг/г) была почти в два раза выше, чем для Amberlite IRC-748 (120,0 мг/г). Материалы с содержанием сшивающего агента 2,5-5% мас. образуют полимерные гели с высоким водопоглощением. Максимальное набухание показали материалы, содержащие 2,5% мас. сшивающего агента (≥ 1400% для сополимера DCF/акриловая кислота и ≥ 1700 для сополимера DCF/метакриловая кислота.). Эти материалы можно рекомендовать в качестве поглотителей воды.

Ключевые слова: 2,5-фурандикарбоновая кислота, сложные эфиры, сополимеры, прочность, ударная вязкость, ионно-обменные свойства

2,5–FURANDICARBOXYLIC ACID DICINAMIL ETHER AND NEW COPOLYMERS ON ITS BASIS

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A method for the synthesis of dicinamyl ester of 2,5-furandicarboxylic acid (DCF) a new unsaturated compound of the furan series and potential monomer for producing copolymers with various vinyl compounds and based on them a new generation of construction and ion-exchange materials has been developed. DCF does not form homopolymers as in bulk as in solution (toluene solvent). However, DCF is actively copolymerized with styrene, methyl methacrylate, methacrylic and acrylic acids to form cross-linked polymers with varying degrees of crosslinking. The copolymerization constants of DCF with all investigated vinyl compounds were determined. The DCF copolymers are enriched with comonomer units for all ratios of the components in the initial reaction mixture. They are statistical, and the comonomer units in the macromolecule are randomly arranged. Copolymers with styrene or methyl methacrylate have higher mechanical strength compared to polystyrene and polymethyl methacrylate. Copolymers containing carboxyl groups and 10-20 % wt. crosslinking agent exhibit good ion-exchange properties with respect to heavy metals. The equilibrium adsorption amount of Cu^{2+} onto ion-exchange copolymers (221-234 mg/g) was almost twice as large as that onto Amberlite IRC-748 (120.0 mg/g). Materials with a crosslinking agent content of 2.5-5% wt. form polymer gels with high water absorption. Materials containing 2.5 % wt. crosslinking agent (≥ 1400 % for copolymer DCF /acrylic acid and ≥ 1700 for copolymer DCF/methacrylic acid) are showed maximum swelling. These materials can be recommended as water absorbers.

Key words: 2,5-furandicarboxylic acid, esters, copolymers, strength, resilience, ion exchange properties

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INTRODUCTION

In recent years, polymers and copolymers based on nitrogen and oxygen-containing vinyl and allyl monomers have found application in various fields of industry, medicine and agriculture. Due to their unique properties these materials are characterized by high mechanical strength, thermal and chemical stability, and good insulating and adhesive properties [1, 2]. Polymers and copolymers of allyl compounds containing polar groups, for example carboxyl, are used as ion-exchange materials, adsorbents and water absorbers [1, 3, 4]. Some allyl monomers are used for crosslinking or curing of polyolefins (grafted copolymerization). Thermosetting products with high heat resistance are produced from crosslinked polymers and copolymers of allyl ethers. Other applications of these polymers are production of casting sheets, molding materials, electrical and optical devices with high resistance and refractory materials [5, 6].

Homopolymerization of diallyl compounds often leads to the formation of low molecular weight products and/or has a cyclic-linear nature, which leads to the production of macromolecules with alternating cyclic and linear units, as well as cyclic structures [6, 7]. The main reason for the formation of low molecular weight homopolymers is the destructive transfer of the chain to the monomer and the cyclization reaction. The behaviour of allyl monomers in copolymerization reactions often is determined by their low reactivity compared to most vinyl monomers. In addition, most allyl monomers are derived from petroleum, for example, diallyl phthalates, diallyl adipates, diallyl maleates, etc [1, 8]. Currently, there is a tendency to replace non-renewable fossil raw materials for the synthesis of valuable chemical products, including monomers and polymers of various classes, with renewable bio-raw materials [9, 10]. Therefore, it is of great interest to search for new allyl monomers that are distinguished by sufficient reactivity and the possibility to be obtained from bio-renewable plant materials.

Previously, 5-hydroxymethylfurfural (HMF) was synthesized by catalytic dehydration of plant hexose-containing raw materials [11]. 2,5-furandicarboxylic acid (FDCA) was prepared by HMF oxidation [12]. Based on FDCA, a new allyl monomers of diallyl-5,5-oxybis-(methylene)bis[furan-2-carboxylate] (DADF) and diallylfuran-2,5-dicarboxylate (DAF) were synthesized and their radical copolymerization with butyl methacrylate was studied [13].

This article reports results on the synthesis of a new furan-based allylic monomer – dicinamyl ester of 2,5-furandicarboxylic acid (DCF). The results of the copolymerization reaction of DCF with unsaturated acids (acrylic acid (AAc), methacrylic acid (MAAc)), styrene (S) and methyl methacrylate (MMA) are studied.

EXPERIMENTAL PART

2,5-Hydroxymethylfurfural and 2,5-furandicarboxylic acid were obtained from bio-renewable raw materials according to previously developed methods [11, 12]. Other Aldrich reagents were used without further purification.

Method for the synthesis of dicinamyl ether FDCA (DCF) from FDCA dichloride.

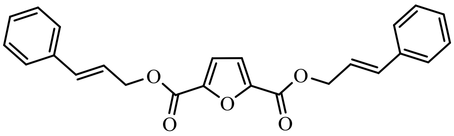

Fig. Structural formula of dicinamyl ester of 2,5-furandicarboxylic acid (DCF) molecule

Рис. Структурная формула молекулы дицинамилового эфира 2,5-фурандикарбоновой кислоты (DCF)

1.92 g (0.01 mol) of FDCA dichloride, 5 ml (0.06 mol) of pyridine and 8 g (0.06 mol) of cinnamic alcohol are placed in a 50 ml round bottom flask equipped with a magnetic stirrer and reflux condenser. The mixture is kept in a silicone bath at a temperature of 30-35 °C within ~ 2 h. At the end of the synthesis, the reaction mixture was cooled to room temperature and diluted with cold water (100 ml) to remove pyridine. The yellowish crystals are separated by filtration and washed with ether (2×10 ml) from excess alcohol. The crystals are dried in air and recrystallized from heptane. The obtained white needle crystals were separated on a Schott filter, washed with cold heptane (~ 3 ml) and dried in air. 3.1 g of dicinamyl ether 2,5-FDCA (DCF) (80%), melting point 88-89 °C (from heptane) was obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 6.9 Hz, 2H), 7.40-7.25 (m, 4H), 6.77 (d, J = 15.9 Hz, 1H), 6.40 (dt, J = 15.8, 6.6 Hz, 1H), 5.02 (d, J = 6.5 Hz, 2H).

General procedure for bulk or solution homopolymerization of DCF. A mixture of 5 g of DCF and 5 mg azo-bis-dinitrile isobutyric acid (AIBN) (0.1 % wt.) was prepared in a wide tube. For solution homopolymerization, 5 ml of toluene is added. The reaction mixture was purged with argon for 5 min. After that the tube was closed and heated in an oil bath at 80 °C for 10 h. Then the reaction mixture was cooled to room temperature, the contents were transferred to a flask and treated with heptane (10 ml). The mixture is placed in the refrigerator (temperature – 20 °C), after 3-4 h. The precipitated crystals are filtered off. The result is the initial monomer, in almost the same amount that was taken for the reaction (3.9-3.95 g). The structure was confirmed by GC-MS and NMR spectroscopy.

General procedure for the synthesis of DCF copolymers with vinyl compounds. In a wide test tube, a mixture of DCF (the amount in wt. % is indicated in Tables 2-5), the corresponding vinyl monomer – unsaturated acid (MAAc, AAc) or styrene or MMA – and AIBN (0.1% wt., 5 mg) was prepared. The total weight of the monomer mixture was 5 g. The reaction mixture was purged with an inert gas (argon or helium) for 2 min, the tube was closed with a ground stopper and heated in an oil bath at 80 °C for 3-8 h (depending on the cross-linked agent content, Table 2-5). Then the mixture is cooled to room temperature, the polymer is recovered, which is a solid glassy mass.

The control samples of polystyrene (PS), polymethyl methacrylate (PMMA), polyacrylic (PAAc) and polymethacrylic (PMAAc) acids were obtained under the same conditions (the initiator is AIBN 0.05%, reaction temperature 80 °C).

The methodology for determining the composition of the copolymer and the copolymerization constants. The acid value (AV) of copolymers with MAAc or AAc was determined by titration of copolymers solutions in dimethyl formamide with a 0.1 M alcohol solution of KOH. Methanol or ethanol for copolymers with a high acid content and benzene for copolymers with a high content of DCF can also be used as a solvent. The vinyl monomer content (X_1, %) in the copolymers with unsaturated acids (MAAc or AAc) was calculated based on the AV, and in the copolymers with styrene or with MMA, based on the ether value (EV) [14].

$$X_1 = \frac{AV_{exp}}{AV_{theor}} \cdot 100; \; X_1 = \frac{EV_{exp}}{EV_{theor}} \cdot 100\%$$

The calculation of the copolymerization constants was carried out by the method of intersecting straight lines [15, 16].

Gas chromatography-mass spectrometry (GHMS) was carried out on an Agilent 7890A chromatograph equipped with an Agilent 5975C mass selective detector (EU, 70 eV) and an HP-5MS capillary column.

To confirm the structure of the obtained compounds, ^{1}H and ^{13}C NMR spectroscopy were used. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III spectrometer with operating frequencies of 400.13 and 100.63 MHz, for ^{1}H and ^{13}C nuclei, respectively. Solvent signals served as an internal standard.

The swelling degree and the rate constant of the swelling of the comonomers were determined by the gravimetric method in an LSU instrument in distilled water, toluene and chloroform. Each sample was weighed before the experiment and immersed in an appropriate solvent. Volume changes were measured every 30 min. The duration of the experiment was 240 min at room temperature for each sample. The swelling degree was calculated:

$$\alpha = \frac{\Delta V \rho}{m_0} 100\%,$$

where *ΔV* is the volume of solvent absorbed by the polymer, ρ is the density of the solvent, m_0 is the initial mass of the polymer sample.

Determination of the exchange capacity of the copolymers was carried out according to GOST 20255.1-89. Strength properties of the samples were determined in accordance with [17], hardness was determined according to GOST 24621-2015 (ISO 868: 2003), impact strength according to DIN EN ISO 179-2:1999.

RESULTS AND DISCUSSION

The bulk copolymerization reactions of DCF with styrene, MMA, MAAc and AAc were researched. The calculated values of the copolymerization constants show that, for all monomer ratios in the initial reaction mixture, all 4 series of new copolymers are enriched with comonomer units, in particular, the PS/DCF copolymer is enriched with styrene units, the MMA/DCF copolymer is enriched with MMA units, AAc/DCF and MAAc/DCF copolymers with AAc and MAAc units, respectively. This is evidenced by the ratio of the copolymerization constants ($r_1 < 1$ and $r_2 \geq 1$) (Table 1). In almost all cases, the product of the copolymerization constants ($r_1 \times r_2$) is close to 1 that indicates that the copolymers PS/DCF, PMMA/DCF, AAc/DCF and MAAc/DCF are statistical ones and the comonomer units in the macromolecule are randomly distributed [18].

Table 1

Copolymerization constants of DCF with unsaturated acids, styrene and MMA

Таблица 1. **Константы сополимеризации DCF с непредельными кислотами, стиролом и MMA**

Comonomer	r_1	r_2	$r_1 \times r_2$
AAc	0.5	2.2	1.1
MAAc	0.55	1.7	0.94
Styrene	0.7	1.4	0.98
MMA	0.6	1.55	0.93

The yield and properties of the obtained copolymers depending on the DCF content are presented in Tables 2-5.

In the presence of DCF, the polymerization time of styrene and MMA decreases. And the higher the comonomer content, the shorter the reaction time. So already at a monomer content of 1% wt. the polymerization time was reduced by almost 2 times. The polymerization time of 8 h instead of 18 for pure PS (Table 2) and 14 h for PMMA (Table 3) was observed. When the DCF content was reached 20% wt the copolymerization time was reduced by 5 times (only 4 and 3 h for PS/DCF and PMMA/DCF, respectively).

The PS/DCF and PMMA/DCF copolymers containing 1-2.5% wt. DCF partially retain their solubility in chlorinated hydrocarbons (chloroform, methylene chloride), similar to FDCA diallyl ether copolymers [13]. When the content of DCF ≥ 2.5% wt. crosslinked copolymers are formed that result in losing their solubility in organic solvents completely and their swelling becomes limited. The swelling degree is quite large and amounts to 2400% and 2300% for PS/DCF and PMMA/DCF, respectively. With a further increasing the DCF content in the reaction mixture (20 and 30% wt.), the number of crosslinks increases, and the swelling degree decreases significantly (for PS/DCF – more than 10 times and 2-3 times for PMMA/DCF) (Tables 2, 3).

At a low DCF content (1-5% wt.), the PS/DCF and PMMA/DCF copolymers retain almost the same stiffness as the PS and PMMA control samples. As the amount of DCF increases, the degree of branching of the macromolecules increases too, the copolymer hardness decreases, and the elasticity increases. So at a high content in the initial mixture (20-30% by weight) DCF acts as a plasticizer to sharply decrease stiffness and glass transition temperature of the PS/DCF and PMMA/DCF copolymers (Tables 2, 3).

The obtained copolymers can be proposed to replace polydiallyl phthalate and its copolymers with styrene or MMA [1, 19, 20], which are used for manufacturing of products that require exceptional dimensional stability, ease of molding, low water absorption, and excellent optical and electrical properties.

The copolymers of DCF and unsaturated acids AAc/DCF and MAAc/DCF with a low content of a crosslinking agent of 1% wt. partially soluble in water. If DCF content ≥ 2.5% wt. copolymers have a cross-linked structure and swell to a certain limit, but do not dissolve, therefore, can be used as water absorbers [3, 21]. With an increase in the DCF content to 10%, the number of crosslinks in the polymer increases [13], the limiting swelling decreases several times to no more than 200%. It makes them suitable for use as ion-exchange resins [22].

The study of the ion-exchange properties of copolymers of DCF with unsaturated acids showed that the introduction of 2.5 to 10% wt. DCF does not significantly effect on the exchange capacity (EC) of these resins (Tables 4, 5). The highest exchange capacity was observed for DCF copolymers with unsaturated acids containing 2.5% comonomer (8.0 mEq/g Na$^+$ and 278 mg/g Cu^{2+} for AAc/DCF copolymer). However, these materials are not suitable for ion-exchanging applications because of high swelling degree (for the AAc/DCF and DCF/MAAc α are 1400 and 1700%, respectively). Copolymers containing 10% wt. of DCF with a swelling degree of up to 250% can be recommended as ion-exchangers with EC ≥ 220 mEq/g for Cu^{2+}. Their exchange capacity is not inferior to industrially used ion-exchange resins (KU-2.8, EC = 1.8-2.0 mEq/g; Amberlite IRC-748, EC = 4-4.5 mEq/g) [23].

Table 2

The yield and properties of the copolymer of DCF and styrene, depending on the content of the cross linking agent

***Таблица 2.* Выход и свойства сополимера DCF и стирола в зависимости от содержания сшивающего агента**

DCF content, % wt.	0	1	2.5	5	7.5	10	20	30
Polymerization time, h	18	8	8	6	6	5	4	4
Yield*, %	100	100	100	100	99	99	92	89
Stiffness	hard	hard	hard	hard	hard	hard	elastic **	elastic **
Glass transition temperature, °C	100	105	108	114	122	130	110	93
Swelling in CHCl$_3$, %	dissolves	partially dissolves	partially dissolves	2400	1800	1150	720	220
Shore hardness, HB	637	637	520	318	305	300	160	90
Half decomposition temperature, °C	350	360	364	367	372	375	376	377
Tensile strength, MPa	40.1	50.3	55.4	57.6	56.1	53.4	43.2	25.8
Impact strength, kJ/m^2	3.0	4.6	5.1	7.9	8.0	8.3	10.5	13.2

Notes: * – the rest is a comonomer that has not reacted;
** - quickly restores shape after deformation
Примечания: *– остальное сомономер, не вступивший в реакцию;
** – быстро восстанавливает форму после деформации

Table 3

The yield and properties of the copolymer of DCF and MMA depending on the content of the cross linking agent

***Таблица 3*. Выход и свойств сополимера DCF и MMA в зависимости от содержания сшивающего агента**

DCF content, % wt.	0	1	2.5	5	7.5	10	20
Polymerization time, h	14	8	8	6	6	5	3
Yield*, %	100	100	100	100	99	99	92
Stiffness	hard	hard	hard	hard	hard	elastic **	plastic
Glass transition temperature, °C	104	108	110	113	123	98	27
Swelling in CHCl$_3$, %	dissolves	slightly soluble	slightly soluble	2300	2000	1300	940
Shore hardness, HB	637	637	530	316	308	220	40
Half decomposition temperature, °C	213	225	-	242	-	254	255
Tensile strength, MPa	76.0	91.2	93.6	95.4	82.6	73.9	43.7
Impact strength, kJ/m^2	15.0	18.5	19.2	20.3	21.5	21.8	22.2

Notes: * – the rest is a comonomer that has not reacted;
** - quickly restores shape after deformation
Примечания: *– остальное сомономер, не вступивший в реакцию;
** – быстро восстанавливает форму после деформации

Table 4

The yield and properties of copolymers of DCF and acrylic acid depending on the content of the cross linking agent
Таблица 4. **Выход и свойства сополимеров DCF с акриловой кислотой в зависимости от содержания сшивающего агента**

DCF content, % wt.	0	1	2.5	5	7.5	10	20
Polymerization time, h	6	3	3	2	2	2	1
Yield, %	0	100	100	100	99	99	97
Stiffness	hard	hard	hard	hard	hard	hard	hard
Glass transition temperature, °C	106	108	110	113	118	133	150
Swelling in water, %	dissolves	slightly soluble	1400	1100	670	220	90
EC, mEq/g Na^{2+}	-	-	8.1	7.8	7.2	7.0	6.3
EC, mg/g Cu^{2+}	-	-	278	266	254	248	234
Half decomposition temperature, °C	637	637	637	637	637	637	637
Tensile strength, MPa	351	362	370	393	413	421	423
Impact strength, kJ/m^2	2.5	2.3	1.8	1.7	1.6	1.3	0.6

Table 5

Yield and properties of copolymers of DCF and methacrylic acid depending on the content of the cross linking agent
Таблица 5. **Выход и свойства сополимеров DCF с метакриловой кислотой в зависимости от содержания сшивающего агента**

DCF content, % wt.	0	1	2.5	5	7.5	10	20
Polymerization time, h	6	3	3	2	2	2	1
Yield, %	0	100	100	100	99	99	98
Stiffness	hard	hard	Hard	hard	hard	hard	fragile
Glass transition temperature, °C	227	231	233	242	258	269	273
Swelling in water, %	dissolves	slightly soluble	1700	1400	800	250	110
EC, mEq/g Na^{2+}	-	-	7.5	7.1	6.5	6.2	5.9
EC, mg/g Cu^{2+}	-	-	256	246	238	231	221
Half decomposition temperature, °C	637	637	637	637	637	637	637
Tensile strength, MPa	308	324	339	363	372	388	397
Impact strength, kJ/m^2	2.8	2.5	1.9	1.6	1.3	0.8	0.3

CONCLUSION

The synthesis of a new furan-based monomer – dicinamyl ether of 2,5-furandicarboxylic acid (DCF) was carried out. The processes of its homopolymerization and copolymerization with styrene, methyl methacrylate and unsaturated acids (acrylic, methacrylic) were studied. DCF does not form homopolymers in both bulk and solution (toluene solvent), but reacts with all studied monomers to form copolymers with varying degrees of crosslinking. The copolymerization time of binary systems decreases with increase of the DCF crosslinking agent.

The copolymerization constants of DCF with unsaturated acids, styrene and methyl methacrylate were determined. The DCF copolymers are enriched with comonomer units for all ratios of the components in the initial reaction mixture. They are statistical ones, and the comonomer units in the macromolecule are randomly arranged.

The formation of three-dimensional polymers with all the studied compounds is confirmed by the loss of their solubility in the corresponding solvents (chloroform, carbon tetrachloride, toluene for copolymers with styrene and methyl methacrylate; water for copolymers with acrylic and methacrylic acids) and the ability to limit swelling.

For copolymers with acrylic or methacrylic acid, the copolymer stiffness increases with increase in DCF cross-linking agent, and with a high DCF content (more than 20% wt.) the material becomes fragile. For copolymers of styrene or methyl methacrylate, an increase in the DCF content, on the contrary, leads to a decrease in stiffness and an increase in heat resistance. The increase in elasticity is explained by the plasticizing effect of DCF, similar to the action of diallyl phthalate.

The ion-exchange properties of copolymers containing carboxyl groups with respect to sodium and heavy metals have been studied. As ion-exchange materials, unsaturated acids copolymers with DCF 10% wt. can be used. These copolymers showed the swelling degree required for ion-exchange materials (not more than 250% wt.) at a high exchange capacity (≥ 6 mEq/g for Na^+). These copolymers can be recommended for removing heavy metals ions from wastewater. They are good adsorbents with respect to copper ions (221 and 234 mg/g for MAAc/DCF and AAc/DCF copolymers respectively).

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