UDC 547.541:542.913

SYNTHESIS OF NEW THERMOSTABLE POLYHYDROXYESTER ON THE BASIS OF 2-HYDROXYPROPYL-1,3-*BIS*-CARBOXYMETHYLESTEROSULFOIMIDE OF SACCHARIN-6-CARBOXYLIC ACID

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Received 17.03.2023
Accepted 11.04.2023

Abstract: *By polycondensation of 2-hydroxypropyl-1,3-bis-carboxymethylesterosulfoimide of saccharin-6-carboxylic acid with ethylene glycol, a thermostable polyhydroxyester was obtained. The structure of the synthesized compound was confirmed by data of the infrared spectroscopy and the thermal stability studied by a method of differential-thermal analysis on a derivatograph of "Paulik—Paulik Erdei" system. The derivatographic investigations showed that the synthesized polyhydroxyester had high thermal stability and physical-mechanical properties.*

Keywords: *monomer, 2-hydroxypropyl-1,3-bis-carboxymethylesterosulfoimide of saccharin-6-carboxylic acid, polyhydroxyester*
DOI: 10.32737/2221-8688-2023-2-140-145

Introduction

As is known, the polyesteroimides (PEI) are heterocyclic polymers, in which the aromatic rings are alternated with ester and imide groups. The high solubility of PEI favors the preparation of low-viscosity solutions with high polymer content. These solutions are used as lacquers. PEIs form the hard, elastic films stable to heat and possessing electrical isolating properties. A characteristic peculiarity of such films is their stability to simultaneous mechanical and thermal action [1].

As compared to aromatic PEIs, the aromatic polyesterosulfoimides (PESI) possess improved solubility, fire-, thermal- and radiation resistance [2,3].

Previously, the chloroanhydrides of disaccharindicarboxylic acid, diesterosulfoimides [4, 5], dialkyl esters of N-carboxymethylsaccharin-6-carboxylic acid and diimides of disaccharindicarboxylic acid had been used as monomers for preparation of highly thermostable PESI in the polycondensation reaction with aliphatic and aromatic amines, diols and dichloroorganic compounds.

There are data in the literature that the polyhydroxyesters (PHE) are characterized by such practically valuable properties as high adhesion to various surfaces, thermal stability, chemical resistance, low affinity to water. Owing to the free hydroxyl groups located along all length of the polymer chain, PHEs are able to cure, undergo the reaction with various substances – amines, acids, chloroanhydrides, etc. They are well combined with various organic and mineral fillers, which can be used for preparation of various polymer composites.

PHEs are valuable polymer materials used as the base of glues, lacquers, film-forming substances in a number of branches of technology. Unlike low molecular weight epoxypolymers, the high molecular weight ones are thermoplastic linear polymers with high content of the hydroxyl groups. The production of such polymers was mastered on an industrial scale in some countries [6-8].

All things considered, the aim of the work is the synthesis of new thermostable polymers

on the basis of sulfoimide-containing monomers.

With that consideration, we have synthesized the sulfoimide-containing PHE by a method of polycondensation.

Experimental part

Synthesis of 2-hydroxypropyl-1,3-*bis*-carboxymethyl esterosulfoimide of saccharin-6-carboxylic acid. In a three-necked round-bottomed flask the mixture consisting of 25.5 g (0.05 mol) of 2-hydroxypropyl-1,3-*bis*-esterosulfoimide of saccharin-6-carboxylic acid, 14 g (~0.1 mol) of powdered potassium carbonate, 9.5 g (~0.1 mol) of monochloroacetic acid and 50 g CI was dissolved in 260 ml of DMAA and boiled for 8 hours. Upon completion of the reaction, the obtained mass was cooled to room temperature; the fallen crystals were washed twice with DMAA and filtered through Schott filter. The synthesized substance was dried at room temperature and then in vacuum to a constant mass.

Synthesis of polyhydroxyester sulfoimide of saccharin-6-carboxylic acid. 12.52 g (0.02 mol) of 2-hydroxypropyl-1,3-*bis*-carboxymethylesterosulfoimide of saccharin-6-carboxylic acid previously dissolved in 1.24 g (0.02 mol) of 1,2-ethanediol and 0.1 g of PbO was loaded into glass reactor equipped with a thermometer, a mechanical stirrer, a capillary and a nitrogen feeding pipe. The mixture was heated to 175 -180°C.

As a result of re-esterification, the methanol was isolated. Then, the temperature was raised to 220°C and the remaining methanol isolated for 1.5 hours. Upon completion of the reaction, the mass was washed with distilled water, and then the polymer was precipitated firstly with ethyl alcohol, then with acetone. The obtained substance was dried under vacuum to a constant mass.

The physical-chemical properties of solvents were in line with the literature data [9, 10].

The infrared spectra were taken on the IR-Fourier spectrometers LUMOS and ALPHA (BRUKER Germany) in the wave frequency range 600-4000 cm^{-1}, using the NPVO prefix with ZnSe crystal. The crystal diameter is 1 cm. A number of the sample scans is 24, the measurement duration is 30 sec.

The elemental analysis was carried out according the method [11] based on pyrolytic combustion of the organic substance in oxygen flow using the Pregl apparatus.

The thermal stability of the obtained compounds was studied by a method of differential- thermal analysis on derivatograph of Paulik-Paulik-Erdei system [12, 13]. Sample weighing – 200 mg, channel sensitivity TG–200, DTA–250 μv, DTG –1 mv, temperature rise rate – 5°C/min in the air current.

Ostwald glass viscometers were used for measurement of the characteristic viscosity. The solvent flow time was from 46 to 120 sec. The concentration dependences of the reduced viscosity $\eta_{rd}/s = (t/t_0 - 1)/s$ were constructed for a number of samples. The Huggins constant values were determined by the slope of the experimental lines:

$$H_{rd}/s = [\eta] + k'[\eta]^2 s,$$

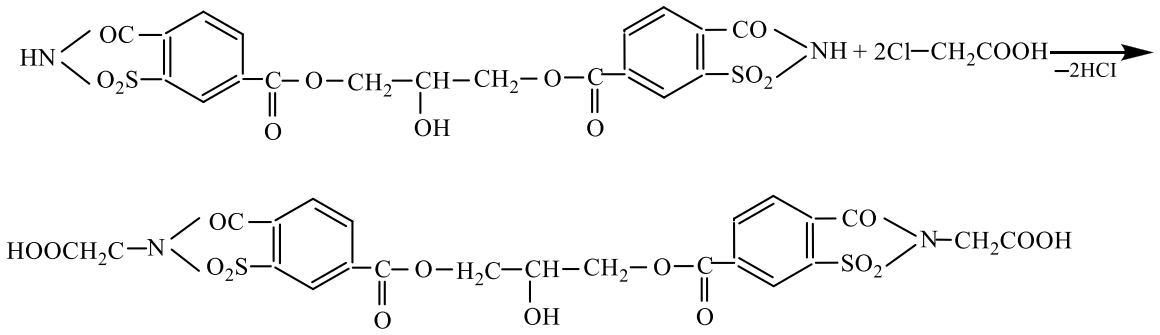
where k' – Huggins constant, which characterizes the thermodynamic interaction of the solvent and polymer, as well as the hydrodynamic behavior of the solution. The error of determination of [η] value does not exceed 5 percent.

The study of physical-mechanical properties was carried out on a breaking machine WPM, VEB Thuringerindustriewerk, Rauenstein R-40, ТУР-2092.

Results and discussion

The synthesis of new hydroxyl-containing polyesterosulfomide-polyhydroxyester (PHE) of sulfoimide of saccharin-6-carboxylic acid was carried out in two stages.

At the first stage, as a result of the interaction of 2-hydroxypropyl-1,3-*bis*-esterosulfoimide of saccharin-6-carboxylic acid with monochloroacetic acid, 2-hydroxypropyl-1,3-*bis*-carboxymethyl esterosulfoimide of saccharin-6-carboxylic acid (2-HP-1,3-*bis*-CMES of S-6-CA) was synthesized according to the following scheme [14]:



It revealed that the obtained product was a light coffee-colored powder, soluble only in aprotic solvents, such as DMFA, DMAA, DMSO, etc.

The yield of the purposeful product was 78.6 %.

The composition and structure of 2-HP-1,3-*bis*-CMES of S-6-CA were determined by means of the elemental analysis and IR-spectroscopy.

Table 1. Physical constants of 2-HP-1,3-*bis*-CMES of S-6-CA

Compound	Brutto formula	Found,% / Calculated,%				MW	M.p. °C	Yield, %
		C	H	N	S			
2-HP-1,3-*bis*-CMES of S-6-CA	$C_{23}H_{18}O_{15}N_2S_2$	57.95 / 58.79	2.14 / 2.87	1.61 / 2.24	9.81 / 10.22	626	190	78.6

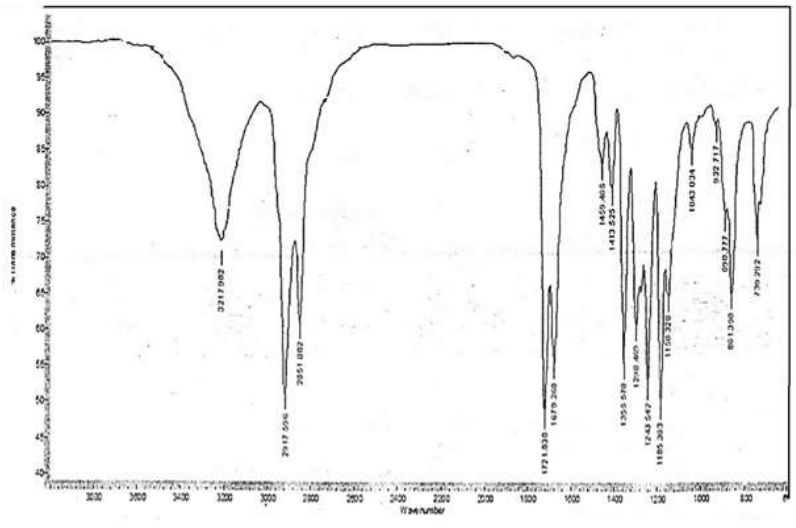
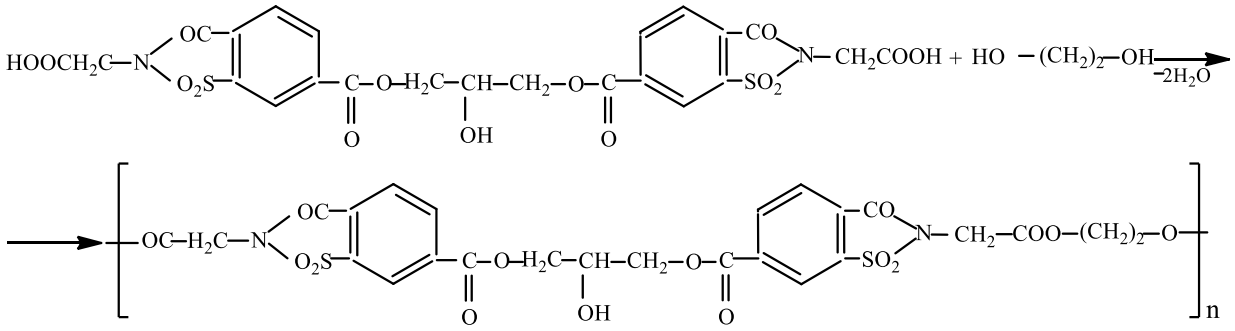


Fig. 1. IR spectrum of 2-HP-1,3-*bis*-CMES of S-6-CA.

It was established that in the IR spectra (Fig.1) of this compound there were absorption bands in the field of 1355, 1413, 1459 cm^{-1} of the deformation vibrations of C-H bond of CH_2 group; valence vibrations of C=O-bond of acid groups in the field of 1721 cm^{-1}; valence vibrations of COOH-group in the field of 2851, 2917 cm^{-1}; valence vibrations of amide C = O-

bond in the field of 1679 cm^{-1}; valence vibrations in the field of 1243, 1298 cm^{-1} of C-N-bond; valence vibrations of C-O- and O-H-bonds of alcohol in the fields of 1043 cm^{-1} and 3217 cm^{-1}; valence vibrations of SO_2-bond in the field of 1150, 1185 cm^{-1}; deformation vibrations of C-H-bond (739, 861, 890 cm^{-1}) of substituted benzene ring [15-17].

At the second stage, by interaction of the obtained compound with ethylene glycol (1,2-ethanediol), new PHE of sulfoimide of saccharin-6-carboxylic acid has been synthesized according to the following scheme [18]:



The yield of purposeful product was 77%.

It was established by IR spectroscopy that in the IR spectra of this compound there are absorption bands in the field of 2918 cm^{-1} of the deformation vibrations of C–H bond of CH_2 group; valence vibrations (1107 cm^{-1}) of C–O bond of ester; valence vibrations of C=O-bond of acid groups in the field of 1726 cm^{-1}; valence vibrations of amide C=O-bond in the field of 1644 cm^{-1}; valence vibrations in the field of 1286 cm^{-1} of C-N-bond; valence vibrations of C-O- and O-H-bonds of alcohol in the field of 1052 and 3254 cm^{-1}; valence vibrations of SO_2-bond in the field of 1248; deformation vibrations of C-H-bond (761 cm^{-1}) and valence vibrations of C-C-bond (1534 cm^{-1}) of substituted benzene ring.

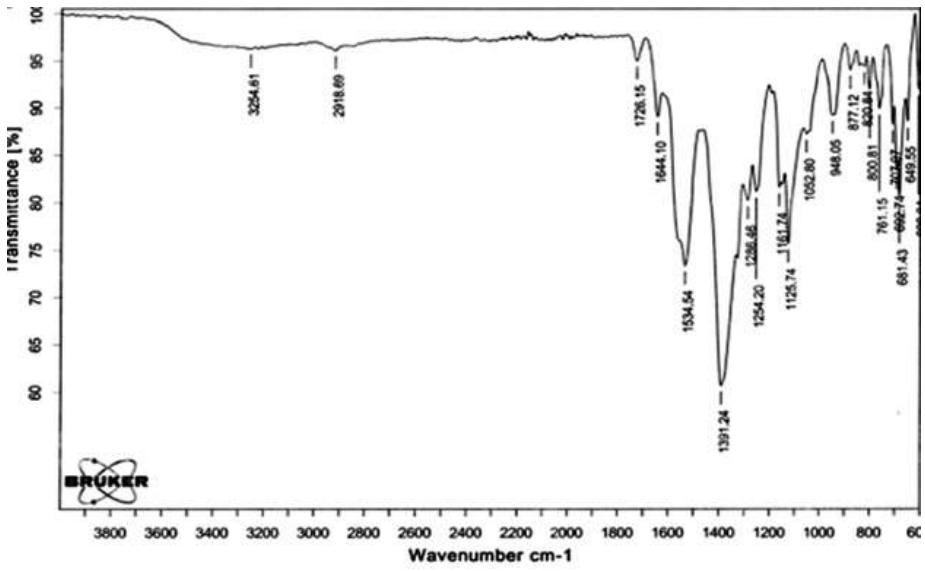


Fig. 2. IR spectrum of PHE of S-6-CA

It was experimentally proved that the viscosity of the obtained PHE of S-6-CA corresponds to [η]=0.62 dl/g.

It was established on the basis of differential-thermal analysis (DTA) data that the synthesized PHE was thermally stable in the interval of 228-255°C and is well dissolved in polar aprotic solvents.

According to the physical-mechanical parameters, PHE has the following data: elongation, ε – 5%, tensile strength, σ_p - 105 MPa.

The synthesized PHEs of sulfoimide of saccharin-6-carboxylic acid are of interest for their use in the production of glues, thermostable coatings and films, as well as polymer composites.

References

1. Borodulin A.S., Kalinnikov A.N., Muzyka S.S., Tereshkov A.G. Polyesteroimides for the creation of heat-resistant polymer composition materials with high physical-mechanical properties. *Herald of V.G. Shukhov BSTU*. 2019, no. 11, pp. 94–100.
2. Rusanov A.L., Prigozhina M.P., Komarova L.G., Shevelev S.A., Dutov M.D., Serushkina O.V. New sulfur-containing aromatic diamines and related soluble polyimides. *Polymer Science*, series A. 1999, vol. 41, no. 1, pp. 65–68.
3. Wei-Feng Peng, Huan-Yu Lei, Xin-Xin Zhang, Lu-Hao Qiu. Fluorine Substitution Effect on the Material Properties in Transparent Aromatic Polyimides. 2022, *Chinese Journal of Polymer Science (English Edition*). 2022, April, vol. 40(7), pp. 1-8.
4. Tatli Mehmet. Facile Synthesis of Functionalized Poly (Arylene Ether Sulfone)s. Dayton: Wright State University, Department of Chemistry. 2012.
5. Aslanov T.A. Synthesis of polyamide (estero)sulfimides by a method of polycondensation. *Azerb. Chem. Journal*. 2005, no. 4, pp. 116119.
6. Beeva D.A., Mikitaev A.K., Beev A.A., Olkhovaya G.G. Synthesis of polyhydroxyesters on the basis of bisphenol A. *Modern science-consuming technologies*. 2004, no. 1, pp. 81-82.
7. Bezgin V.S., Kochergin Yu.S. Structural melt glues on the basis of polyhydroxyester *Herald of Donbass National Academy of Construction and Architecture*. 2014, no. 1(105), pp. 133–138.
8. Aslanova E.T. Synthesis of polyhydroxy-esters of sulphoimide sakharin-6-carbonic acid *Chemical problems*. 2019, vol. 17, no. 4, pp. 571–575.
9. Gordon A., Ford R. Sputnik khimika. Moscow: Mir Publ., 1976. 546 p.
10. Kiper R.A. Physical-chemical properties of substances: Handbook of Chemistry. Khabarovsk. 2013. 1016 p.
11. Balandina V.A., Gurvich D.B., Klesheva M.S., Bezugly V.D. Analysis of polymerization plastics. Moscow-Tashkent: Chemistry Publ., 1965. 512 p.
12. Wendlandt U. Thermal methods of analysis. Moscow: Mir Publ., 1978. 527 p.
13. Kurenkov V.F. Workshop on chemistry and physics of polymers. Moscow: Khimiya Publ., 1990. 299 p.
14. Aslanova E.T. Rashidova M.N. Garayeva A.A. Heydarova S.Y. Atakishiyeva V.O. Synthesis of some derivatives of 2-hydroxypropyl-1,3-*bis*-ester-sulphoimide of saccharin-6-carboxylic acid. *Az. Chem. Journal*. 2022, no. 4, pp. 78–82.
15. Kazitsina L.A., Kupletskaya N.B. Application of UV, IR, NMR and mass spectroscopy in organic chemistry. Moscow: MSU Publishing House, 1979, 236 p.
16. Tarasevich B.N. IR spectra of the main classes of organic compounds. Moscow. 2012. 54 p.
17. Prech E., Bulmann F., Affolter K. Determination of the structure of organic compounds. Moscow: Mir Publ., 2006, 438 p.
18. Aslanov T.A., Salakhov M.S., Efendiev A.A. Polyestersulfimides on the basis of dimethyl esters of saccharin-6-dicarboxylic acids and aliphatic diols. *Polymer Science, series* B. 2005, vol. 47, no. 3, pp. 65–67.

SAXARİN-6-KARBON TURŞUSUNUN 2-HİDROKSİPROPİL-1,3-*BİS*-KARBOKSİMETİLEFİROSULFOİMİDİ ƏSASINDA YENİ TERMİKİ DAVAMLI POLİHİDROKSİEFİRİN SİNTEZİ

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Xülasə: Saxarin-6-karbon turşusunun 2-hidroksipropil-1,3-bis-karboksimetilefirosulfoimidinin etilenqlikolla polikondensasiyası nəticəsində termiki davamli polihidroksiefir alınmışdır. Sintez edilmiş birləşmənin strukturu İQ-spektroskopiya vasitəsi ilə təstiq edilmişdir. Termiki stabillik "Paulik-Paulik-Erdey" sistemli derivatoqrafda differensial-termiki analiz üsulu ilə öyrənilmişdir. Derivatoqraf tədqiqatları göstərmişdir ki, sintez edilmiş polihidroksiefirlər yüksək termiki stabilliyə və fiziki- mexaniki göstəricilərə malikdirlər.

Açar sözlər: monomer, saxarin-6-karbon turşusunun 2-hidroksipropil-1,3-bis-karboksimetil-efirosulfoimidi, polihidroksiefir

СИНТЕЗ НОВОГО ТЕРМОСТОЙКОГО ПОЛИГИДРОКСИЭФИРА НА ОСНОВЕ 2-ГИДРОКСИПРОПИЛ-1,3-*БИС*-КАРБОКСИМЕТИЛЭФИРОСУЛЬФОИМИДА САХАРИН-6-КАРБОНОВОЙ КИСЛОТЫ

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Аннотация: Поликонденсацией 2-гидроксипропил-1,3-бис-карбоксиметилэфиро-сульфоимида сахарин-6-карбоновой кислоты с этиленгликолем получен термостойкий полигидроксиэфир. Структура синтезированного соединения подтверждена данными инфракрасной спектроскопии. Термическую стабильность изучали методом дифференциально-термического анализа на дериватографе системы «Паулик-Паулик-Эрдей». Дериватографические исследования показали, что синтезированный полигидроксиэфир обладает высокой термостабильностью и физико-механическими показателями.

Ключевые слова: мономер, 2-гидроксипропил-1,3-бис-карбоксиметилэфиросульфоимид сахарин-6-карбоновой кислоты, полигидроксиэфир