

SYNTHESIS OF POLYHYDROXYESTERS OF SULPHOIMIDE SAKHARIN-6-CARBONIC ACID

E.T. Aslanova

*Institute of Polymer Materials
National Academy of Sciences of Azerbaijan
124, S. Vurgun str., AZ 5004 Sumgayit, Azerbaijan; e-mail:elnara-aslanova@rambler.ru*

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Abstract: Heat-resistant polyhydroxyesters were obtained through polycondensation of 2-hydroxypropyl-1,3-bis-ester of sulfoimide saccharin-6-carboxylic acid with some aliphatic diamines. Structures of the synthesized compounds were confirmed by infrared spectroscopy data. Thermal stability was studied by means of differential thermal analysis on a derivatograph of the Paulik-Paulik-Erdei system. Derivatographic studies showed that the synthesized polyhydroxyethers have a high thermal stability which decreases as a length of the aliphatic fragment in their composition increases. X-ray studies went to show that the obtained compounds were amorphous polymers.

Keywords: saccharin-6-carboxylic acid, diamine, polyhydroxyether

Introduction

As is known, polyhydroxyethers (PHE) are characterized by practically valuable properties, specifically high adhesion to various surfaces, thermal stability, chemical resistance, low affinity for water. Owing to free hydroxyl groups located along the entire length of the polymer chain, PHE can cure and react with various substances – amines, acids, acid chlorides, etc. They are well combined with various organic and mineral fillers that can be used to obtain various polymer composites.

Note that PHEs are valuable polymeric materials used as the basis of adhesives, varnishes, film-forming substances in several engineering industries. In contrast to low molecular weight, epoxy polymers with high molecular weight are thermoplastic linear polymers with a high content of hydroxyl groups. The production of these polymers has been commercialized in some countries [1, 2].

From the literature it is known that complex polyetherimides have high heat resistance and, unlike polyimides, are easily processed [3]. Compared to aromatic polyimides, aromatic polysulfoimides have an improved solubility, flame, thermal and radiation resistance [4-6]. Granting this, the purpose of the work is to synthesize new thermo-resistant polyhydroxyesters based on sulfoimide of saccharin-6-carboxylic acid.

On the basis thereof, we were the first to synthesize sulfoimide-containing PHE by means of polycondensation.

Experimental part

Materials. We used *m*-cresol ("Biochem", France); ethylenediamine (Neftegazkhimkomplekt LLC, Russia); tetramethylenediamine (Topan LLP, Kazakhstan); Hexamethylenediamine (Topan LLP, Kazakhstan); ethanol (Bakikimyacezasanaye LLC, Azerbaijan); acetone ("high purity", "Himed Synthesis").

Synthesis of polyhydroxy esters of sulfoimide saccharin-6-carboxylic acid based on diamines. The flask was charged with 5.1 g (0.01 mol) of 2-hydroxypropyl-1,3-bis-ester-sulfoimide saccharin-6-carboxylic acid, 2.24 g (0.02 mol) of EDA-ethylenediamine, dissolved in 60 ml of *m*-cresol. The reaction mass, while stirring, was heated at 160-170 °C for 7 h. Then the

mass was filtered, then washed with distilled water and besieged sequentially with ethanol and acetone; dried in vacuum to constant weight.

Polyethersulfoimides derived from tetramethylenediamine (2) and hexamethylenediamine (3) were synthesized in the same way.

Physico-chemical properties of solvents were consistent with literature data [7].

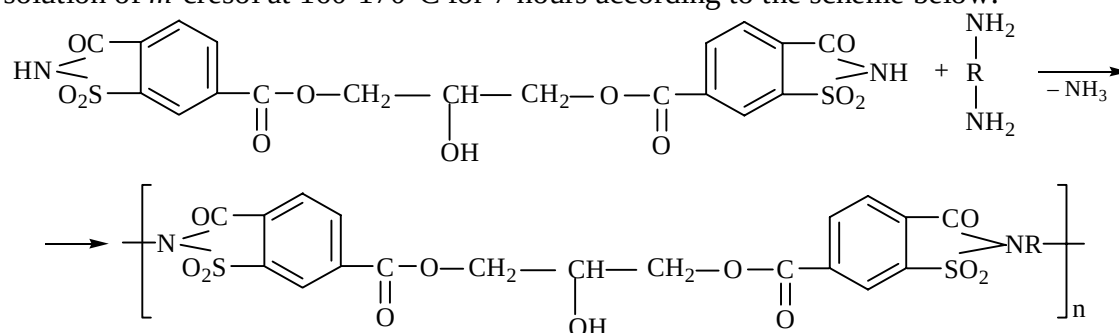
Also, infrared spectra were recorded on a Fourier transform infrared spectrometer LUMOS (BRUKER company Germany) in a wave frequency range of 600-4000 cm^{-1} , using the ATR adapter with a ZnSe crystal. Crystal diameter is 1 cm. The number of sample scans is 24; measurement time is 30 seconds [8, 9].

The thermal stability of the obtained compounds was studied by means of differential thermal analysis on a derivatograph of the "Paulik-Paulik-Erdey" system [10, 11]. Sample weight is 200 mg, sensitivity of TG – 200, DTA – 250 μv channels, DTG – 1 mv, temperature rise rate is 5° C / min in air flow.

Results and discussion

Synthesis of PHE of saccharin-6-carboxylic acid sulfoimide was performed on the basis of previously obtained 2-hydroxypropyl-1,3-bis-ester-sulfoimide saccharin-6-carboxylic acid (2-HP-1,3-bis-ESIS-6-CA) incorporating ester and sulfoimide groups, as well as aliphatic diamines [12].

The polycondensation reaction of 2-HP-1,3-bis-ESIS-6-CA with diamines was carried out in a solution of *m*-cresol at 160-170°C for 7 hours according to the scheme below:



where: R = (CH₂)_n, n = 2, 4, 6

It revealed that the IR spectra of the synthesized compounds contain absorption bands in a range of 1398, 1454 cm^{-1} deformation and 2852, 2922 cm^{-1} valence vibrations of C–H bond of the CH₂ group; C–H high-plane deformation (679, 750, 864 cm^{-1}) vibrations of the substituted benzene ring; deformation (1457, 1628 cm^{-1}) vibrations of the benzene ring; C–O stretching (1015 cm^{-1}) vibrations of alcohol; stretching (1718 cm^{-1}) C = O vibrations of the ester group; C–O stretching (1240 cm^{-1}) vibrations of the ester bond; stretching (1156, 1340 cm^{-1}) vibrations of SO₂ groups; and C–N valence (1240, 1283 cm^{-1}) vibrations. The broad and intense absorption band in a range of 3200-3550 cm^{-1} with a maximum of 3300 cm^{-1} refers to the stretching vibrations of associated hydroxyl groups.

Phase state and morphology largely determine the physico-chemical properties of polymers, they are essential to understand processes in the course of operation and processing of materials [13]. There is no data on the phase state of PHE in the literature; therefore, the work in this area is of particular interest. Radiographic studies of PHE were performed using an automatic diffractometer of the "Drone" type (fig. 1) in the step-scan mode using X-rays with a wavelength of 1.7888Å. The obtained X-ray patterns revealed in all samples of synthesized PHE the presence of amorphous ring while the absence of peaks in the crystalline phase allows us to define them as completely amorphous polymers. As an example, Fig.1 shows that the radiograph of polyhydroxyester of sulfoimide of saccharin-6-carboxylic acid was synthesized on the basis of tetramethylenediamine.

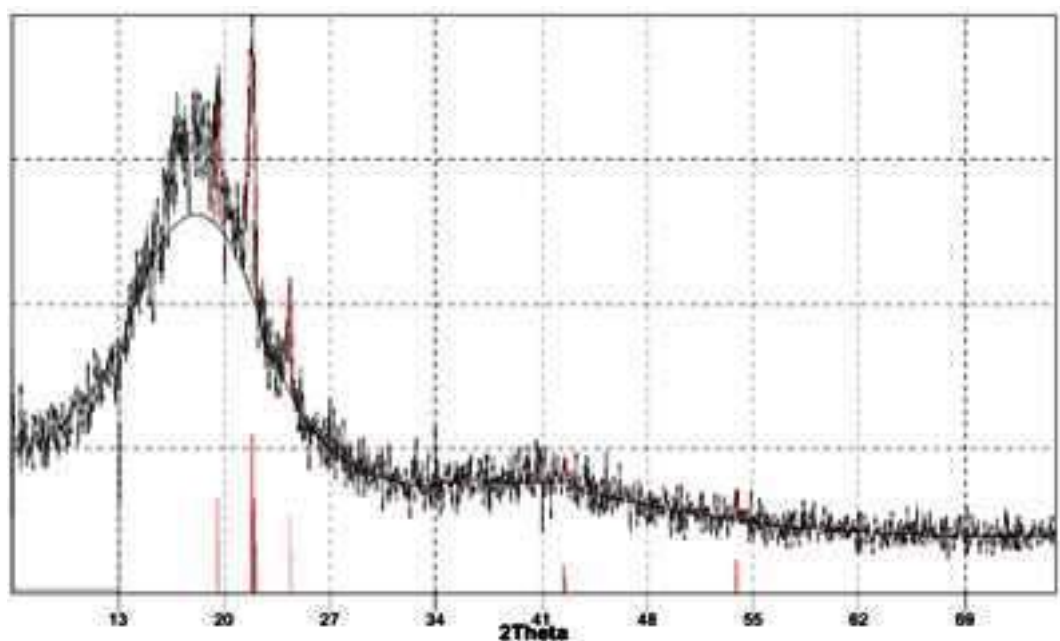


Fig.1. Radiograph of polyhydroxyesters of sulfoimide of saccharin-6-carboxylic acid synthesized on the basis of tetramethylenediamine

According to the differential thermal analysis (DTA) data, it found that the synthesized PHEs are thermo-stable in the range of 237-265°C and are well soluble in polar aprotic and phenolic solvents.

The characteristics of PHE (1-3) is given in Table 1.

Table 1. Some characteristics of polyhydroxyesters of composition 1-3.

Polymer	Output, %	$[\eta]^*$, dl/g	Softening temperature, °C	Decomposition starting temperature, °C
1.	70.0	0.55	235	265
2.	72.0	0.60	223	250
3.	75.0	0.67	215	237

*0.5 g of polymer in 100 ml of DMF at 40°C

As is seen from Table 1, the obtained compounds can be arranged in terms of thermal stability depending on the used diamine: ethylenediamine (1)>tetramethylenediamine (2)>hexamethylenediamine (3).

Note that synthesized PHE of sulfoimide saccharin-6-carboxylic acids are of interest from standpoint of their use in the production of adhesives, heat-resistant coatings and films.

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SAXARİN-6-KARBON TURŞUSUNUN SULFOİMİDİNİN POLİHİDROKSİEFİRLƏRİNİN SİNTEZİ

E.T. Aslanova

*Azərbaycan Milli Elmlər Akademiyası Polimer Materialları İnstitutu,
AZ 5004, Sumqayıt, S.Vurğun küşəsi, 124
E-mail: elnara-aslanova@rambler.ru*

Saxarin-6-karbon turşusunun 2-hidroksipropil-1,3-bis-efirosulfoimidinin bəzi alifatik diaminlərlə polikondensləşdirilməsindən termiki davamlı polihidroksiefirlər alınmışdır. Sintez olunmuş birləşmələrin quruluşu infraqırmızı spektroskopiya üsulu ilə təsdiq edilmişdir. Termiki sabillik differensial-termiki analiz üsulu ilə "Paulik-Paulik-Erdey" sistemli derivatoqrafda öyrənilmişdir. Derivatoqrafik tədqiqatlar göstərdi ki, sintez olunmuş polihidroksiefirlər yüksək termiki sabilliyə malikdirlər, onların termiki sabilliyi tərkibindəki alifatik fraqmentin uzunluğu artdıqca azalır. Rentgenoqrafik tədqiqatlarla sübut edilmişdir ki, alınmış birləşmələr amorf polimerlərdir.

Açar sözlər: *saxarin-6-karbon turşusu, diamin, polihidroksiefir*

СИНТЕЗ ПОЛИГИДРОКСИЭФИРОВ СУЛЬФОИМИДА САХАРИН-6-КАРБОНОВОЙ КИСЛОТЫ

Э.Т. Асланова

*Институт Полимерных Материалов Национальной АН Азербайджана
AZ 5004 Сумгайыт, ул. С. Вургуна, 124
E-mail: elnara-aslanova@rambler.ru*

Поликонденсацией 2-гидроксипропил-1,3-бис-эфиросульфоимида сахарин-6-карбоновой кислоты с некоторыми алифатическими диаминами получены термостойкие полигидроксиэфиры. Структуры синтезированных соединений подтверждены данными инфракрасной спектроскопии. Термическую стабильность изучали методом дифференциально-термического анализа на дериватографе системы «Паулик-Паулик-Эрдей». Дериватографические исследования показали, что синтезированные полигидроксиэфиры обладают высокой термостабильностью, уменьшающейся по мере роста длины алифатического фрагмента в их составе. Рентгенографическими исследованиями доказано, что полученные соединения являются аморфными полимерами.

Ключевые слова: сахарин-6-карбоновая кислота, диамин, полигидроксиэфир