# Synthesis Methods of Saccharin-6-Carboxylic Acid Triglyceride

E.T. Aslanova

Institute of Polymer Materials of the Azerbaijan National Academy of Sciences, Sumgait

***Abstract*****—** *One and two-step methods for the synthesis of saccharin-6-carboxylic acid triglyceride were studied. The reesterification reactions of 2-hydroxypropyl-1,3-bis-ethersulfoimide of this acid and glycerol with some aliphatic saccharin-6-carboxylic acid esters were carried out. The resulting products are characterized by elemental analysis and IR spectroscopy and size exclusion chromatography. It was found that when using a two-step method, the end product is obtained with the highest yield (85%).*

***Keywords*****— alkyl esters, glycerine, IR-spectra, monomer, reesterification, saccharin-6-carboxylic acid.**

## I. INTRODUCTION

Aromatic and aliphatic polysulfoimides (polysaccharines) are sulfur-containing analogues of polyimides. Polysulfoimides differ from polyimides by the presence in the imide cycle of one carbonyl (C=O) and one sulfonyl (-$SO_2$-) group [1]. These polymers possess high thermal stability (500-650°C), solubility, stability to radiation and light, acid and alkaline hydrolysis [2].

Polymer composite materials made based on compounds which contain epoxy and sulfoimide groups have high physicomechanical and thermal properties [3]. Epoxyimide oligomers possess the highest heat resistance, in which glycidyl groups are directly adjacent to the imide cycle [4]. In this regard, they are widely used as high-strength and heat-resistant construction materials.

It is known that epoxy resins, in particular dianes, are used after the introduction of hardening agents. Considering that the majority of epoxy composite materials in hardened form have brittleness that impairs the physicomechanical properties of the obtained material, often compounds with a plasticizing property are introduced into the composition, for example, esters and compounds containing groups capable of hardening by epoxy groups of the resin [5-7].

In this regard, given the advantages of polysaccharines, there is a need to develop effective methods for the synthesis of new monomers (prepolymers) based on saccharin monocarboxylic acids [8]. There is evidence of the use of diimidodicarboxylic acids as monomers in the synthesis of polyetherimides. The properties of these polymers can change due to the introduction of various fragment groups into their molecule [9, 10].

There is data in the literature on the synthesis of diesterodisulfoimides by reesterification of the methyl ester of saccharin-monocarboxylic acids with aliphatic and aromatic glycols [11, 12].

This paper describes one- and two-step methods for the synthesis of saccharin-6-carboxylic acid triglyceride**.**

The aim of the work is the synthesis of new monomers based on saccharin-6-carboxylic acid, for their further use in the preparation of highly branched and net heat-resistant polymers.

## II. EXPERIMENTAL

### 2.1 Synthesis of triglyceride based on 2-hydroxypropyl-1,3-bis-ethersulfoimide saccharin-6-carboxylic acid

A mixture of 20 g (0.039 mol) of 2-hydroxypropyl-1,3-bis-etirosulfoimide of saccharin-6-carboxylic acid, 9.53 g (0.039 mol) of saccharin-6-carboxylic acid methyl ester and 2 g of PbO in 200 ml of DMF at stirring was heated to 124°C for 2 hours. The reaction mass was washed with acetone, the end product was isolated from the reaction medium as a precipitate by precipitation with distilled water.

The obtained coffee-milk colour powder product was dried at room temperature and brought to constant weight in vacuum. $T_m$ =167°C.

Similarly, the above mentioned compounds were synthesized based on saccharin-6-carboxylic acid ethyl and isopropyl esters.

### 2.2 Synthesis of triglyceride by reesterification of aliphatic esters of saccharin-6-carboxylic acid with glycerine

A mixture of 40 g (0.016 mol) of saccharin-6-carboxylic acid methyl ester, 7.5 g of PbO in 4.6 g (0.05 mol) of propane-1,2,3-triol (glycerine) was heated to 115-117°C with stirring for 2 hours. The reaction mass was washed with acetone, and then was isolated as a precipitate by precipitation with distilled water. The obtained coffee-milk colour powder product was dried at room temperature and brought to constant weight in vacuum. Tm =167°C.

In the work, distilled glycerine of the PK-94 brand was used with a mass fraction of pure glycerine of not less than 94.0%. Physicochemical properties of glycerine and solvents are corresponded to the literature data [13].

Infrared spectra were recorded on an infrared Fourier spectrometer LUMOS (firm BRUKER Germany) in the wavelength range of 600-4000 $cm^{-1}$, using an ATR attachment with a ZnSe crystal. The diameter of the crystal is 1 cm. The number of scans of the sample is 24; the measurement duration is 30 seconds.

Elemental analysis was performed according to the method [14], based on the pyrolytic burning of organic matter in an oxygen stream using the Pregl apparatus.

Molecular weights (MW) and molecular weight distribution (MWD) parameters of the synthesized products were determined by size exclusion chromatography (SEC) on the high performance liquid chromatograph (*Kovo, Czech Republic*) with a refractometric detector. Two columns with a size of 3.3 × 150 mm filled with a stationary Separon-SGX phase with a particle size of 7 μm and a porosity of 100 Å were used. Eluent – DMF, flow rate 0.3 ml/min. T=20-25°C. The calibration dependence of *lgM* on the hold-up volume $V_R$ in the range M=(1.5-100)×$10^2$, described by the equation $V_R=C_1-C_2lgM$, where $C_1$=24.4, $C_2$=4, was obtained using PRG standards. The interpretation of MMP chromatograms was performed according to the method [15, 16]. The calculations are carried out according to the equations:

$$M_w=\Sigma M_i\,\omega_i;\ M_n=1/\,\omega_i/\,\Sigma M_i \qquad (1)$$

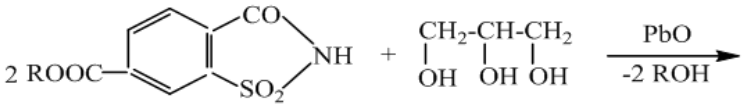
where $M_w$ – weight-average molecular weight, $M_n$ – number-average molecular weight, $M_i$ –molecular weight corresponding to the $i^{th}$ area of the chromatogram, $\omega_i$ – fraction of the area of part *i*.

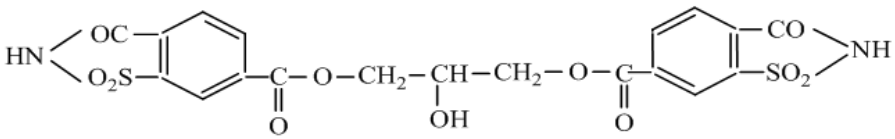
## III. RESULTS AND DISCUSSION

For the synthesis of triglyceride of saccharin-6-carboxylic acid was first applied a method of obtaining on the basis of our previously synthesized 2-hydroxypropyl-1,3-bis-ethersulfoimide saccharin-6-carboxylic acid [17].

The process was carried out in two steps.

In the first step, 2-hydroxypropyl-1,3-bis-ethersulfoimide of saccharin-6-carboxylic acid was obtained:




R= $-CH_3$, $-C_2H_5$, $-C_3H_7$

As a result of reesterification, 2-hydroxypropyl-1,3-bis-ether-sulfosulfoimide of saccharin-6-carboxylic acid was obtained, which included ester and sulfoimide groups [18]. The yield of the end product is 85%.

It was found that the IR spectra of this compound (Fig. 1) contain absorption bands in the regions of 1385, 1434, 1454 $cm^{-1}$ deformation and 2851, 2884, 2921 $cm^{-1}$ valence vibrations of C–H bonds of the $CH_3$ and $_{CH2}$ groups; deformation vibrations (673, 713, 755, 829 $cm^{-1}$) of C–H bond of the substituted benzene ring; deformational vibrations (1487, 1605 $cm^{-1}$) of C–H

bond of the benzene ring; valence vibrations (1039cm$^{-1}$) of C–O bonds of the alcohol; valence vibrations (1719 cm$^{-1}$) of the C=O group of the ester; valence vibrations (1166, 1244 cm$^{-1}$) C–O bond of the ester bond; valence vibrations (1129, 1146, 1278, 1290 cm$^{-1}$) of $SO_2$ groups; and absorption bands at 1643, 1553, 1339 cm$^{-1}$ – amide bands for the H–N–C=O group [19, 20].

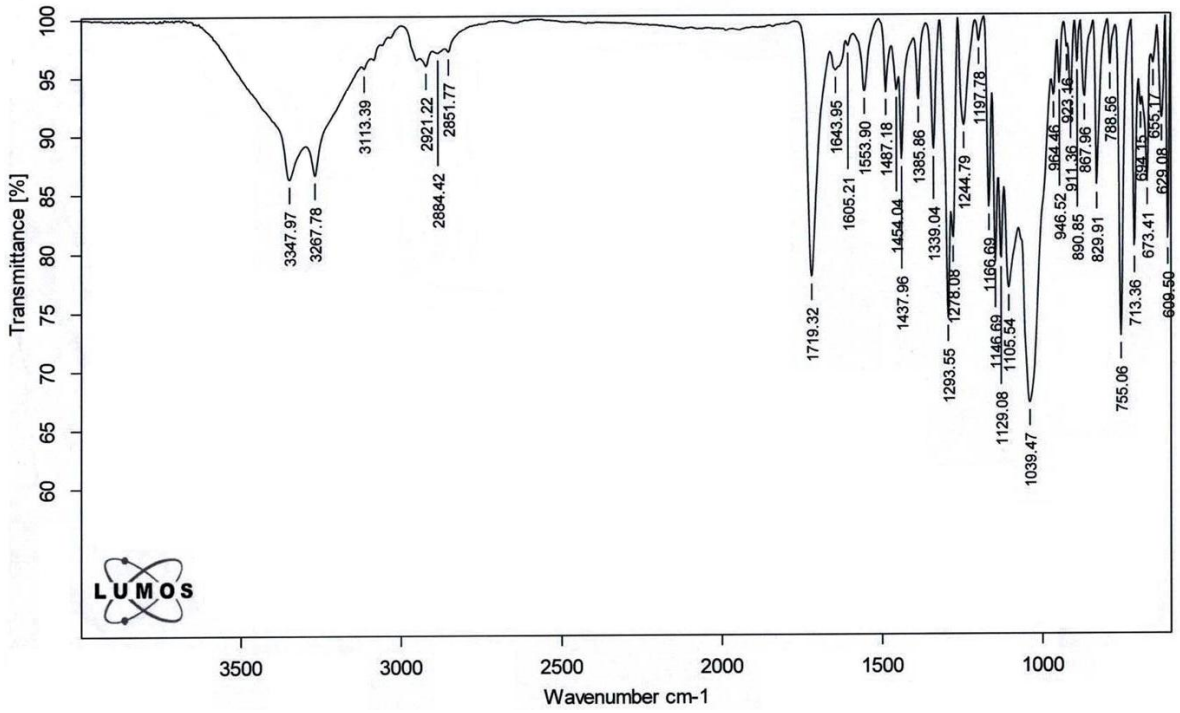
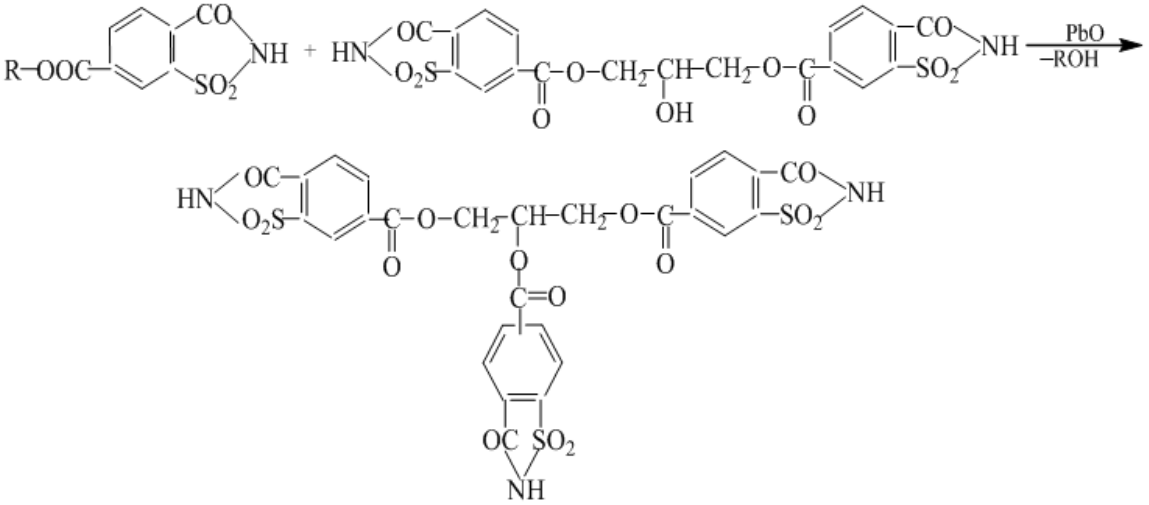



**FIGURE 1: IR spectra of 2-hydroxypropyl-1,3-bis-ether-sulfosulfoimide of saccharin-6-carboxylic acid**

In the second step, by the interaction of the obtained 2-hydroxypropyl-1,3-bis ethersulfoimide with esters of the same acid under more severe conditions, saccharin-6-carboxylic acid triglyceride was synthesized. The reaction proceeded as follows:




R=-$CH_3$,-$C_2H_5$,-$C_3H_7$

The yield of the end product is 85%.

It was found that the obtained product is a light coffee-milk colour powder, soluble only in aprotic solvents such as DMF, DMAA, DMSO, etc.

The composition and structure of the obtained compound was determined by elemental analysis (Table 1) and IR spectroscopy.

**TABLE 1**
**PHYSICAL CONSTANTS OF SACCHARIN-6-CARBOXYLIC ACID TRIGLYCERIDE SYNTHESIZED BY A TWO-STEP METHOD**

| Compound | Empirical formula | Found, % / Calculated, % | | | | M | $T_m$, °C | Yield, % |
|---|---|---|---|---|---|---|---|---|
| | | C | H | N | S | | | |
| saccharin-6-carboxylic acid triglyceride | $C_{27}H_{17}O_{15}N_3S_3$ | 44.95 / 45.06 | 2.48 / 2.36 | 5.81 / 5.84 | 13.43 / 13.35 | 719 | 167 | 85 |

In the IR spectra of the obtained compound (Fig. 2), deformation absorption bands appear in the 1385, 1438, 1485 $cm^{-1}$ region of the C–H bond of the $CH_2$ groups; valence vibrations (1643 $cm^{-1}$) of the C=O bond of the amide; valence vibrations (1719 $cm^{-1}$) C=O of the ester bond; valence vibrations (1108, 1129, 1147, 1168 $cm^{-1}$) of the C–O bond of the ester; valence vibrations (1252, 1277 $cm^{-1}$) of the $SO_2$ group; deformation (1553 $cm^{-1}$) and valence (3268, 3352 $cm^{-1}$) vibrations of the N–H bond; deformation (674, 694, 713, 757, 788, 829, 867, 1607 $cm^{-1}$) vibrations of the C–H bond of the substituted benzene ring.

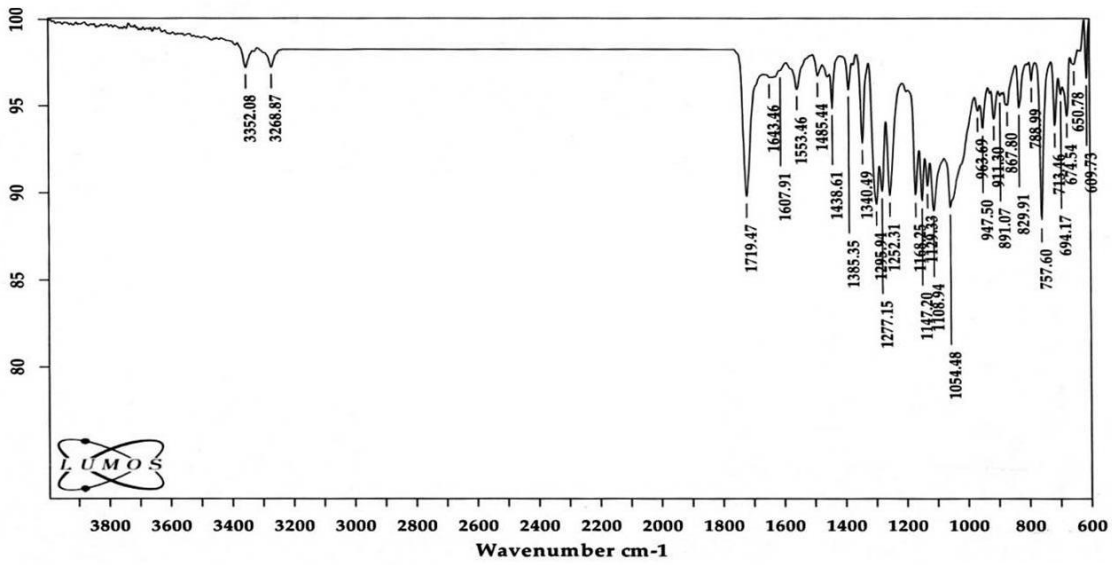
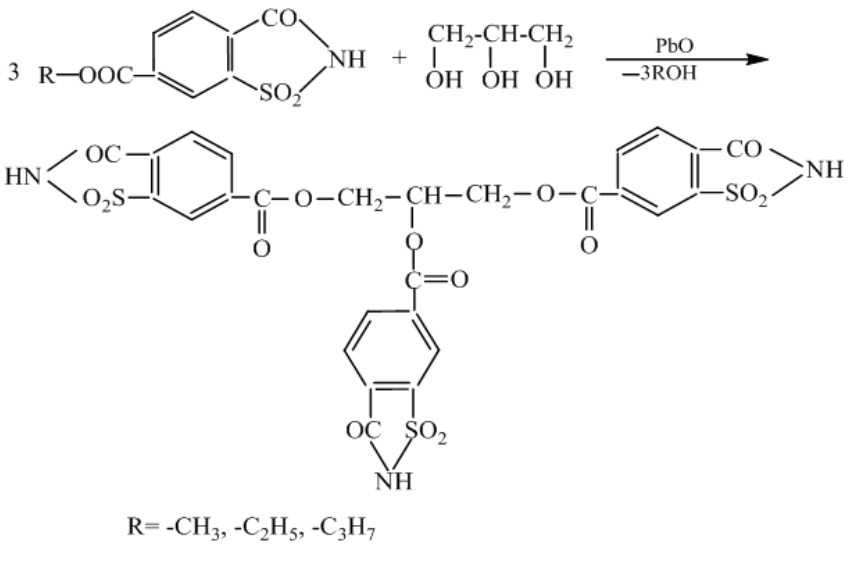



**FIGURE 2: IR spectra of saccharin-6-carboxylic acid triglyceride synthesized by a two-step method**

The one-step synthesis method was carried out by reesterification of saccharin-6-carboxylic acid alkyl esters with propane-1,2,3-triol (glycerol) according to the following scheme:




R= $-CH_3$, $-C_2H_5$, $-C_3H_7$

The obtained product is a light coffee-milk colour powder, soluble only in aprotic solvents such as DMF, DMAA, DMSO, etc.

The composition and structure of the obtained compound was determined by elemental analysis (Table 2) and IR spectroscopy.

**TABLE 2**
**PHYSICAL CONSTANTS of SACCHARIN-6-CARBOXYLIC ACID TRIGLYCERIDE SYNTHESIZED BY a ONE-STEP METHOD**

| Compound | Empirical formula | Found, % / Calculated, % | | | | M | $T_m$, °C | Yield, % |
|---|---|---|---|---|---|---|---|---|
| | | C | H | N | S | | | |
| saccharin-6-carboxylic acid triglyceride | $C_{27}H_{17}O_{15}N_3S_3$ | 44.98 / 45.06 | 2.46 / 2.36 | 5.79 / 5.84 | 13.31 / 13.35 | 719 | 167 | 67 |

The following absorption bands were observed in the IR spectra (Fig. 3) of the obtained compound: deformation (720, 395, 1454 $cm^{-1}$) and valence vibrations of the C–H bond of $CH_2$ groups; valence vibrations (1644 $cm^{-1}$) of the C=O bond of the amide; valence vibrations (1719 $cm^{-1}$) of the C=O bond of the ester; valence vibrations (1153 $cm^{-1}$) of the C–O bond of the ester; valence vibrations (1239, 1283 $cm^{-1}$) of the $SO_2$ group; valence vibrations (1019 $cm^{-1}$) of the S=O bond; deformation (1573 $cm^{-1}$) and valence vibrations (3276 $cm^{-1}$) of the N–H bond; deformation vibrations (617, 678, 750, 859, 1607 $cm^{-1}$) of the C–H bond of the substituted benzene ring.

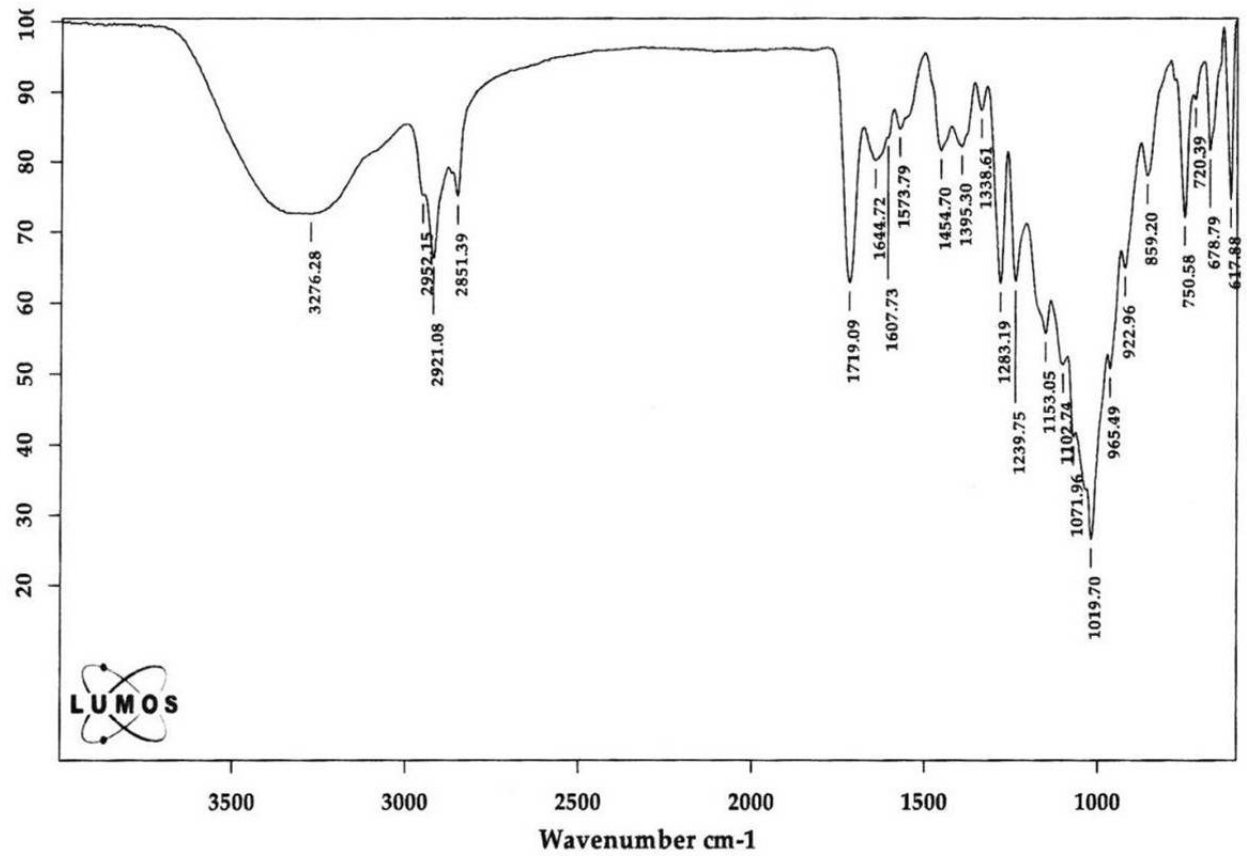



**FIGURE 3: IR spectra of saccharin-6-carboxylic acid triglyceride synthesized by a one-step method**

The identity of the end product is confirmed through molecular weight (MW) by size-exclusion chromatography (Fig. 4). Identical peaks were obtained for triglycerides synthesized by various methods. So the peak recorded at $V_R$ = 15 according to MW corresponds to 220 ($M_{theoretical}$ 222) (lgM=2.35).

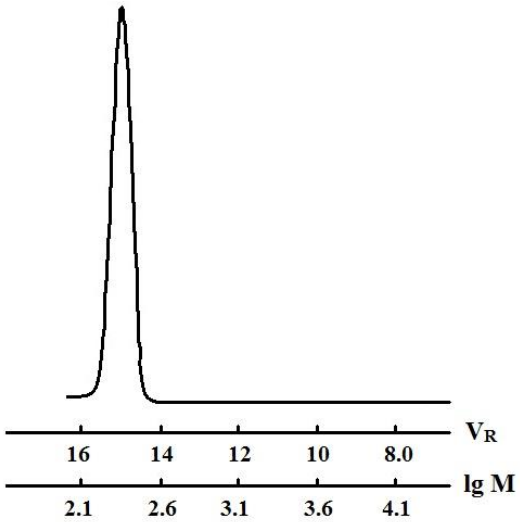



**FIGURE 4: MWD exclusion curve of saccharin-6-carboxylic acid triglyceride. Chromatography conditions: Columns 3.3 × 150 mm, adsorbent: Separon – SGX with a particle size of 7 μm and a porosity of 100 Å. Eluent – DMF, flow rate 0.3 ml / min. Detector: refractometer. 1 count = 0.13 ml**

It should be noted that in order to select the optimal temperature-time regime, the above reaction was carried out under various conditions. With increasing temperature or reaction time, oligomeric products of the same composition were obtained.

## IV. CONCLUSION

Thus, based on the research, the following conclusions can be drawn. One- and two-step methods for the synthesis of saccharin-6-carboxylic acid triglyceride have been developed**;** it was found that in the synthesis of triglyceride by the two-step method, the end product is obtained with the highest yield – 85%; the synthesized saccharin-6-carboxylic acid triglyceride is of interest for its use as a monomer in the production of highly branched and cross-linked sulfoimide-containing polymers and epoxy resins, and also as a hardener-plasticizer of industrial epoxy resins.

## REFERENCES

[1] M. I. Bessonov, M. M. Kotov, V. V. Kudryavtsev, and L. A. Latus, Polyimides – Thermally Stable Polymers. New York: Springer-Verlag, 1987, 318 p.

[2] T. A. Aslanov, M. S. Salakhov, and A. A. Efendiev, "Poly(ester sulfimides) Based on Dimethyl Esters of Saccharin-6-dicarboxylic Acids and Aliphatic Diols," Polymer Science, Series B, vol. 47, pp. 65-67, April 2005.

[3] E. T. Aslanova, T. A. Aslanov, and B. A. Mamedov, "Epoxyimide Compositions On The Basis Of N,N'-Diglycidyl-1,3-Bisesterosulfoimide Of 2-Hydroxypropyl Saccharin-6-Carboxylic Acid," Polymeric Materials and Technologies, Belarus, vol. 3, pp.59-63, April 2017.

[4] L. G. Shode, S. V. Vladimirov, and M. F. Sorokin, "Epoxy imide materials," Paint materials and their application, pp. 20-29, January 1976.

[5] I. Z. Chernin, F. M. Smekhov, and Yu. V. Zherdev, epoxy polymers and compositions. Moscow: Chemistry, 1982, 230 p.

[6] L. Moshinsky, Epoxy resins and hardeners. Tel Aviv: Arcadia Press Ltd, 1995, 370 p.

[7] E. T. Aslanova, T. A. Aslanov, B. A. Mamedov, N. Ya. Ishenko, and E. G. Iskenderova, "2-gidroksipropil-1,3-bis-efirosul'foimid saharin-6-karbonovoj kisloty – otverditel'-plastifikator epoksidnyh smol," Plast.mass, pp. 10-12, September-October 2018 (In Russ)

[8] V.F. Mironov, Monomers for new polymer materials. Moscow: NIITEhim., 1974, 68 p.

[9] B. A. Tagiev, and R. I. Mustafaev, "Sintez polisul'famidoimidov sopolikondensaciej diaminov, disul'fohloridov aromaticheskogo rjada i piromellitovogo diangidrida," Vysokomolek soed. B, vol. 30, pp. 42-45, January 1989. (In Russ)

[10] T. A. Aslanov, M.S.Salakhov, and A.A.Efendiev, "Synthesis of poly(ester sulfoimide) from dichlorocarbonylimide of disaccharindicarboxylic acid and aromatic diols," Journal Appl. Polym. Sci., v. 101, pp. 1687-1691, August 2006.

[11] S. G. Babe, J. de Abajo, and J. Fontan, "Ordered copolyamide-imides and copolyester-imides," Angew. Makromol. Chem., v. 21, pp. 65-67, January 1972.

[12] T. A. Aslanov, U. M. Mamedli, and A.M. Guliev, "Synthesis of Diester Disulfimides from Saccharinmonocarboxylic Acids and Aromatic Diols," Rus. J. Appl. Chem., vol. 78, pp. 441-442, March 2005.

[13] A. Gordon, and R. Ford, Satellite Chemist. Moscow: Mir, 1976, 546 p.

[14] V. A. Balandin, D. B. Gurvich, and M. S. Kleshchev, Analytical Polymerization Plastics. Moscow-Tashkent: Chemistry, 1965, 512 p.

[15] N. R. Bektashi, A. M. Mustafaev, I. A. Guseinov, S. G. Mustafaev and V. D. Dzhafarov, "Chromatographic study of the synthesis of halogenated unsaturated polyesters," Rus. J. Appl. Chem., vol. 84, July 2011.

[16] T. A. Aslanov, E. T. Aslanova, N. R. Bektashi, A. H. Azizov, and Nurullayeva D.R. "1,2-Hydrogen migration in aminoalkyl radicals," European Chemical Bulletin, vol. 5, pp. 495-500, November 2016.

[17] E. T. Aslanova, T. A. Aslanova, A. A. Mamedova, and B. A. Mamedov, "Synthesis of 2-hydroxypropyl-1,3-bis-esterosulphoimides of saccharin-5- and -6-carboxylic acid," Azerb. Chem. J., pp. 45-47, issue 4 2018.

[18] T. A. Aslanov, E. T. Aslanova, F. M. Mamedalieva, and N. Ya. Ishenko, "Synthesis of imide 4-sulfoisophtal acid and its some amide derivatives," Azerb. Chem. J., pp. 54-58, issue 3 2015

[19] L. A. Kazitsina, and N. B. Kupletskaya, Application of UF-, IR -, NMR - and mass spectroscopy in organic chemistry. Moscow: MSU Publishing House, 1979, 236 p.

[20] E. Prech, F. Bulmann, and K. Affolter, Determination of the structure of organic compounds. Moscow: Mir, 2006, 438 p.