Synthesis and Properties of Asymmetric Polyamidosulfoimides on the Basis of Dichloroanhydrides of Saccharin-5-Carboxylic Acids and Aliphatic Diamines

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Abstract**—** *By polycondensation of dichloroanhydride of saccharin-5-carboxylic acids with aliphatic diamines in dimethylacetamide at room temperature the asymmetric polyamidosulfoimide has been synthesized. The influence of nature of solvent, concentration of the initial reagents and reaction temperature on value of characteristic viscosity and also on solubility, thermal stability and deformation-strength properties of the synthesized polyamidosulfoimides has been investigated. It has been elucidated that a growth of a quantity of methylene groups in the polymer leads to the improvement of solubility of the polymers in dimethylformamide and dimethylacetamide, but at the same time leads to the relative deterioration of thermal stability.*

Keywords**— aliphatic diamines, dichloroanhydride of saccharin-carboxylic acids, polyamidosulfoimide, saccharin-5-carboxylic acid.**

I. INTRODUCTION

In recent years, in the field of chemistry of high-molecular compounds, special attention is paid to the development of methods for the synthesis of high-thermostable polymers [1]. The aromatic and aliphatic polysulfoimides (polysaccharins) are the sulphur-containing analogs of polyimides. The polysulfoimides are differed from polyimides by availability of one carbonyl (C=O) and one sulfonyl (-SO_2-) group in imide cycle. These polymers possess high thermal stability (500-650˚C), solubility, resistance to radiation, light, acidic and alkaline hydrolysis.

In this connection, taking into account the advantages of polysaccharins, it is appeared a need of development of the effective methods for synthesis of new monomers on the basis of saccharin-monocarboxylic acids.

It was known that due to solubility in amide solvents and sufficiently high mechanical, thermal and dielectrical properties the polyamidoimides find a wide application in microelectronics in creation of foil-coated dielectrics as the protective coatings. The polyamidoimides prepared on the basis of dichloroanhydrides of dicarboxylic acids possess sufficiently high molecular weight and are differed with thermal stability and also good physical-mechanical properties [2]. There are data about development of method of synthesis of the polyamidoimides containing side carboxyl groups by interaction of imide-containing dichloroanhydrides of dicarboxylic acids with aromatic diamines [3]. We have previously synthesized the symmetric polyamidosulfoimides on the basis of dichloranhydride of saccharin-6-carboxylic acid and aliphatic and also aromatic diamines [4-6].

The purpose of work – synthesis of asymmetric polyamidosulfoimides (PASI) on the basis of dichloranhydrides of saccharin-5-carboxylic acids and aliphatic diamines.

II. EXPERIMENTAL TECHNIQUE

2.1 Synthesis of polyamidosulfoimides

1,2g (0,02 mol) of ethylene diamine and 4,04g (0,04 mol) of triethylamione dissolved in 50ml of DMFA was placed into flask. Then it was added on portions 6,82g (0,02 mol) of dichloranhydride of saccharin-5-carboxylic acid. The reaction was carried out at room temperature for 3 h. At the end of the reaction, the precipitate of hydrochloric triethylamine was filtered, washed with distilled water, the polymer was precipitated by alcohol, then by acetone and was dried in vacuum to constant mass. The polyamidopsulfoimides on the basis of tetramethylenediamine and hexamethylenediamine have been analogously synthesized.

2.2 Film preparation

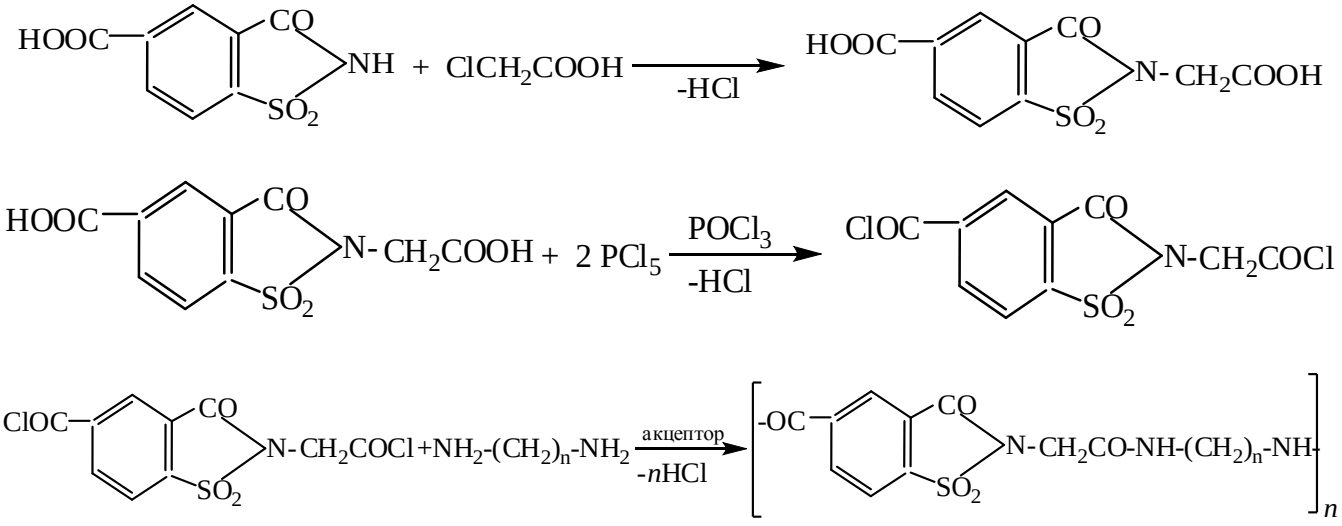
The polyamidosulfoimide films have been prepared from polymer solutions in dimethylformamide; the polymer solution was poured on glass surface and dried at room temperature for 10 h, then was subjected to thermal treatment.

The infrared spectra were taken on IR-Fourier-spectrometer LUMOS (firm BRUKER, Germany) within the range of wave frequencies 4000-600 cm^{-1}, with use of attachment NPVO with crystal ZnSe. A diameter of crystal – 1 cm. A number of scans of the sample –24, measurement duration – 30 s.

The curing process was studied by a method of differential-thermal analysis on derivatograph "Paulik-Paulik-Erdei". The sample hanging – 200 mg, sensitivity of channels – TG-200, DTA-250 μv, DTG-1 mv and temperature rise rate – 5°C /min in current air.

III. RESULTS AND DISCUSSION

For synthesis of the polyamidosulfoimides it was used the method of low-temperature polycondensation in the solvents of amide type, as a result of which the polymers of linear structure with alternating sulfoimide and amide groups in the elementary links have been prepared. The initial reagents for preparation of PASI were dichloranhydride of saccharin-5-carboxylic acid and aliphatic (ethylene-, tetramethylene- and hexamethylene) diamines. The reaction proceeds on the following scheme:



where n=2,4,6

The composition and structure of PASI have been determined by elemental analysis and IR-spectroscopy.

It has been detected that in the IR-spectra of the synthesized compounds there are the absorption bands in the field of 1679 and 1243 cm^{-1}, there are the absorption bands in the field of 3217-3100 cm^{-1}characteristic for >NH group; deformation (739, 861 cm^{-1}) vibrations of C–H bond of substituted benzene ring; deformation (1459 cm^{-1}) vibrations of benzene ring. The absorption in the field of 1721 cm^{-1} is characteristic for C=O bond of carboxylic group. The absorption bands in the field of 1355 cm^{-1} and 1185-1150 cm^{-1}, characteristic for valence vibrations of $–SO_2–$ group in sulfoamides are also observed [7,8]. The valence vibrations at 1298 cm^{-1} are characteristic for C-N bond [7].

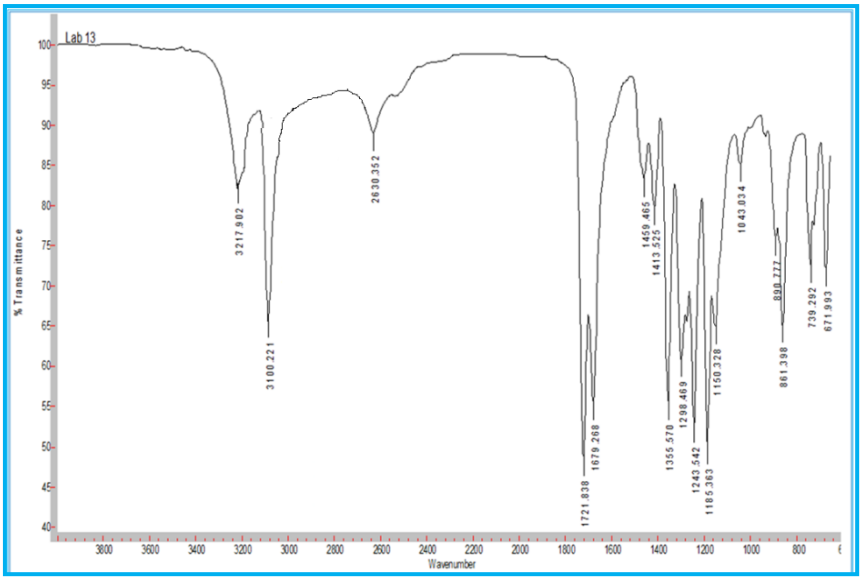


FIGURE 1 . IR SPECTRA OF POLYAMIDOSULFOIMIDES ON THE BASIS OF DICHLOROANHYDRIDES OF SACCHARIN-5-CARBOXYLIC ACID AND ALIPHATIC DIAMINES

The prepared polyamidosulfoimides are the powdery product of yellow color.

It has been investigated the influence of nature of solvent, concentrations of the initial reagents and reaction temperature on value of characteristic viscosity [η]. It has been established that the polymers with the highest viscosity are formed in a medium of dimethylacetamide (DMAA). In this connection, the further polycondensation was carried out in a medium of DMAA.

The nature of the acceptor has also an essential influence on molecular weight of the forming polymer:

Acceptor HCl:	DMAA	Pyridine	$(C_2H_5)_3N$	Na_2CO_3
[η], dl/g	0,22	0,23	0,30	0,55

It was known that DMAA and pyridine are used as the acceptors, but as the carried out investigations showed they are not active enough, as evidenced by the relatively low values of [η]. An application of triethylamine doesn't lead to the polymer preparation with high viscosity, which can be explained by formation of the stable complex of chloranhydride group of DCSCA in DMAA with triethylamine, which complicates the polyamidation. The polyamidosulfoimide with the greatest [η] has been prepared in use of sodium carbonate as an acceptor.

The results of the carried out experiments showed that the highest value of viscosity of the polyamidosulfoimide is reached at 15-20°C. The carrying out of process at lower (5°C) or higher (35-40°C) temperatures leads to a considerable decrease of characteristic viscosity of the polymer. Apparently, this has been connected with stability of complex, forming by chloranhydride group with solvent. At low temperatures this complex is so stable that the reaction with diamine becomes difficult, and at high temperatures the reactive complexes are not generally formed [8].

A concentration of the initial monomers shows also a definite influence; the best values of PASI: [η] 0,51 dl/g (III) have been obtained at concentration of the initial components – 12 mass% (III).

Thus, the optimal conditions of synthesis of the polyamidosulfoimides are as follows: solvent – DMAA, acceptor – sodium carbonate, synthesis temperature – 20°C, reagents concentration – 10-12 mass%. The characteristics of PASI (I- III is presented in Table 1.

It has been found by the methods of DTA and TGA that the decomposition process for these polymers depending on structure for PASI, prepared on the basis of saccharin-5-carboxylic acid is begun at 348-360ºC, and on the basis of saccharin-6-carboxylic acid – at 358-373ºC [9]. The thermogravimetric analyses of the polymer showed that 10%-s mass loss occurs at 385-395ºC (I-III) [10]. On thermal stability the synthesized polyamidosulfoimides depending on used diamine are located in

the following series: ethylene diamine>tetramethylene diamine>hexamethylene diamine.

TABLE 1

SOME CHARACTERISTICS OF THE POLYAMIDOSULFOIMIDES OF COMPOSITION I-III

Polymer	R	Yield, %	[η], dl/g	M.p.,°C	$T_{begin.decom.}$,°C
I.	—$(CH_2)_2$—	80.0	0.46	243	360
II	—$(CH_2)_4$—	82.0	0.48	225	355
III.	—$(CH_2)_6$—	84.0	0.51	207	348

where, I, II, III – data for PASI on the basis of saccharin-5-carboxylic acid

On the basis of synthesized compounds the polyamidosulfoimide films have been prepared. In Table 2 the deformation-strength properties of films prepared from industrial polyamides of composition polyamidoimide-polyvinyl pyrrolidone (PAI-PVP) and synthesized polyamidosulfoimides are presented 2.

TABLE 2

DEFORMATION-STRENGTH PROPERTIES OF FILMS OF COMPOSITIONS I-III AND PAI-PVP

Polymer	R	σ_p, MPa	Δ_ℓ, %
I.	—$(CH_2)_2$—	60	6
II.	—$(CH_2)_4$—	58	8
III.	—$(CH_2)_6$—	55	10
PAI-PVP	–	40	30

As is seen from Table 2, the synthesized polyamidosulfimides on physical-mechanical indices [11] are on the level of the industrial polyamidoimides. These polymers possess also highly film-forming properties.

We have also studied the solubility of the synthesized polyamidosulfoimides in various aprotonic solvents – dimethylformamide and dimethylacetamide. As shown by the results of investigations, the growth of quantity of methylene groups in the polymer leads to the improvement of the polymer solubility, but at the same time, leads to the relative deterioration of the thermal stability.

The synthesized polyamidosulfoimides can be used in electrotechnics as the high-strength coatings holding high temperature regime.

IV. CONCLUSIONS

By polycondensation of dichloroanhydride of saccharin-5-carboxylic acids with aliphatic diamines in dimethylacetamide at room temperature the asymmetric polyamidosulfoimide has been synthesized. It has been established the optimal condition of synthesis of the polyamidosulfimides: solvent – DMAA, acceptor – sodium carbonate, synthesis temperature – 20°C, reagents concentration – 10-12 mass%.

It has been elucidated by methods of DTA and TGA that on thermal stability the prepared compounds depending on used diamine are located in the following series: ethylene diamine>tetramethylene diamine>hexamethylenje diamine. It has been established that the synthesized polyamidosulfoimides possess high physical-mechanical indices. On exploitation indices they are on the level of the industrial polyamidoimides. It has been revealed that the growth of quantity of methylene groups in the polymer leads to the improvement of the polymer solubility in aprotonic solvents, but also to the relative deterioration of their thermal stability.

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