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REGULARITIES OF PREPARATION AND PROPERTIES OF SYMMETRICAL POLYAMIDOSULFOIMIDES

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Abstract. By polycondensation of dichloroanhydride of bisaccharin-dicarboxylic acid with aliphatic diamines, the soluble aliphatic compounds of polyamidosulfoimides (PASI) are synthesized and characterized. The influence of the concentration of the initial reagents and reaction temperature on the yield and characteristic viscosity values of PASI is studied and the optimal condition of synthesis of polyamidosulfoimides is found. It is shown by the methods of DTA and TGA that the synthesized PASIs possess high thermal stability (653–673K) and can be used at higher temperature regimes. At the same time, the special attention is paid to the creation of the polymer materials containing sulfur- and nitrogen-containing fragments in their composition, favoring not only to thermal stability, but also to improvement of solubility and other physical-mechanical parameters.
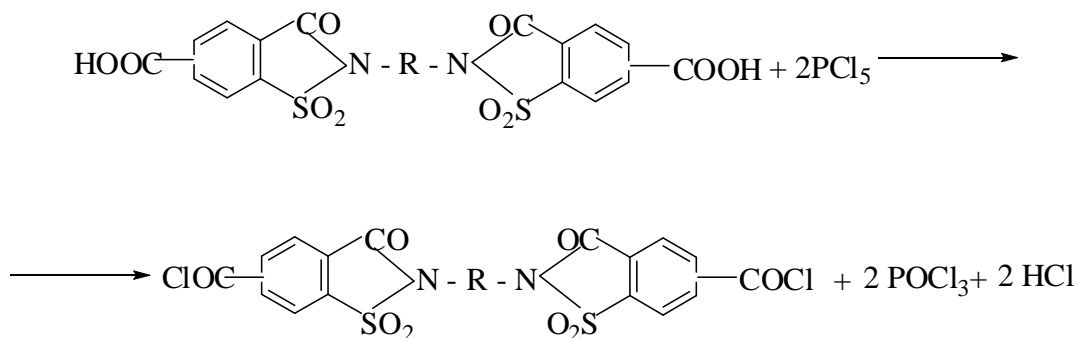
1. Introduction

It is known that the polyamidoimides obtained on the basis of the diimidodicarboxylic acids are differed with high thermal stability, but relatively low molecular weight. Polyamidoimides with high molecular weight are obtained by polycondensation of dichloroanhydrides of diimidodicarboxylic acid with diamines in a medium of the polar solvents (Aslanov *et al.,* 2015).
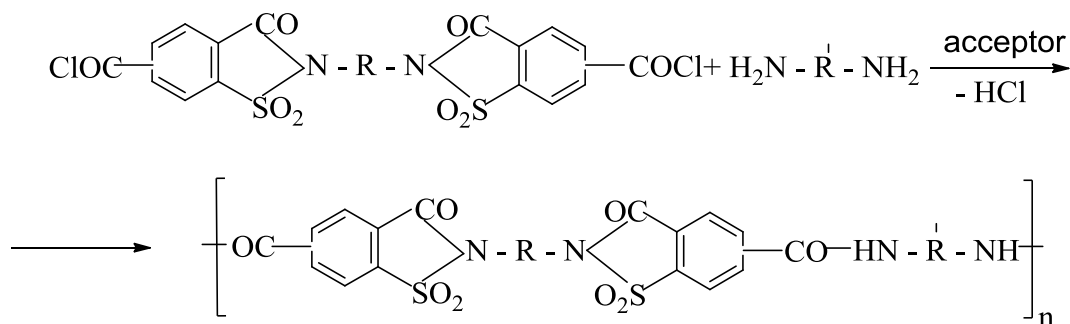
It was of interest to obtain thermo-stable polyamidosulfoimides on the basis of the functional derivatives of disaccharindicarboxylic acids synthesized by us with relatively high molecular weight indices, but having solubility and meltability, i.e. good technological properties.

In this paper, the results of the investigation on the synthesis of polyamidosulfoimides by polycondensation of dichloroanhydride of bisaccharin-dicarboxylic acid with aliphatic diamines are presented. The initial raw material for the preparation of dichloroanhydride of bisaccharin-dicarboxylic acid is taken diacid of bisaccharin-dicarboxylic acid (Aslanova *et al.,* 2019). The reaction occurs according to the following scheme:

$$HOOC - \overset{CO}{\underset{SO_2}{\bigcirc}} N - R - N \overset{OC}{\underset{O_2S}{\bigcirc}} - COOH + 2PCl_5 \longrightarrow$$

$$\longrightarrow ClOC - \overset{CO}{\underset{SO_2}{\bigcirc}} N - R - N \overset{OC}{\underset{O_2S}{\bigcirc}} - COCl + 2 POCl_3 + 2 HCl$$

where, $R = —(CH_2)_2—$; $—(CH_2)_4—$; $—(CH_2)_6—$

Polyamidosulfimides have been synthesized by polycondensation with aliphatic diamines (ethylene-(I), tetramethylene-(II), hexamethylenediamine (III)) on the basis of the obtained dichloroanhydride of bissaccharin-dicarboxylic acid according to the scheme:

$$ClOC - \overset{CO}{\underset{SO_2}{\bigcirc}} N - R - N \overset{OC}{\underset{O_2S}{\bigcirc}} - COCl + H_2N - \overset{'}{R} - NH_2 \xrightarrow[- HCl]{acceptor}$$

$$\longrightarrow \left[OC - \overset{CO}{\underset{SO_2}{\bigcirc}} N - R - N \overset{OC}{\underset{O_2S}{\bigcirc}} - CO - HN - \overset{'}{R} - NH \right]_n$$

where $R = —(CH_2)_2—(I)$; $—(CH_2)_4—(II)$; $—(CH_2)_6—(III)$.

The low temperature polycondensation was carried out in aprotic solvents. As a result of reaction, the polymers of linear structure with alternating sulfoimide and amide groups in the elementary links have been obtained.

2. Experimental part

Synthesis of dichloroanhydrides of bisaccharin-dicarboxylic acid. Dichloroanhydrides of bisaccharin dicarboxylic acid have been synthesized with the addition of 2.5 mole excess of POCl$_3$. The reaction proceeded at 353-358K for 1.5-2 h. At the end of the reaction, the excess of POCl3 was distilled, and the precipitate was filtered out, washed first with dry benzene, and then with chloroform; further the obtained mass was recrystallized from toluene or acetone and dried in a vacuum case at (368-373) K to a constant mass.

Synthesis of polyamidosulfoimides. 2.16 g (0.02 mol) of ethylenediamine, as an acceptor of the isolated HCl carbonate-sodium, dissolved in 50 ml of DMAA was placed into three-necked flask equipped with a stirrer, a chlorocalcium tube and a capillary for feeding of inert gas. After that, 6.32 g (0.02 mol) of dichloroanhydride of bisaccharin-dicarboxylic acid was added in portions. The reaction was carried out at room temperature for 3 h. At the end of the reaction, the mass was washed first with distilled water, the polymer was precipitated with ethyl alcohol, then acetone. Dried in vacuum to a constant weight. Yield – 90.5%.

Similarly, PASIs have been synthesized on the basis of tetramethylenediamine and hexamethylenediamine.

3.   Results and discussion

The synthesized dichloroanhydride of bisaccharin-dicarboxylic acid is a gray powdery product with m.p. 433-435K, soluble in aprotic solvents. In the IR spectra of the synthesized polyamidosulfoimides, the intensive absorption bands of the sulfimide cycle in the field of 1780-1790 cm^{-1} are observed.

The synthesized polyamidosulfoimides are gray powdery products soluble in aprotic solvents. The composition and structure of these compounds are confirmed by the data of elemental analysis and IR spectroscopy. It is detected that in the IR spectra (Fig. 1) of the synthesized compounds there are absorption bands in the fields of 1679-1243 cm^{-1}, characteristic for amide groups. The absorption bands in the field of 1679 cm^{-1} have been stipulated by valence vibrations of C=O group, and in the field of 1243 cm^{-1} – vibrations of >NH group. The absorption band in the field of 1721 cm^{-1} is characteristic for C=O bond of the carboxyl group. In all polyamidosulfoacids, the absorption bands in the field of 1355 cm^{-1} and 1185-1150 cm^{-1}, characteristic for valence vibrations – SO_2– group in sulfoamide fragments are also observed. The absorption bands of the valence vibrations of C-N bond are appeared at 1298 cm^{-1} (Bekhnazarov *et al.,* 2021).
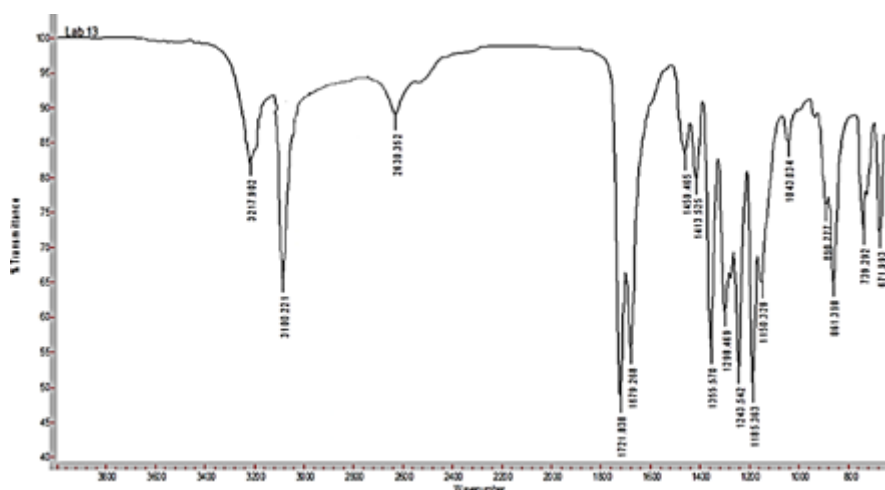

Fig. 1. IR spectrum of polyamidosulfimide

In the synthesis of polyamidosulfoimides, the influence of the nature of the solvent, the concentration of the initial reagents and the reaction temperature on the molecular weight value of polymers is investigated by the example of the polycondensation reaction of dichloroanhydride of bisaccharine-5-carboxylic acid with hexamethylenediamine (Mamedaliyeva, 2019; Rovkina, 2011).

Some kinetic regularities of polycondensation of dichloroanhydrides of bisaccharin-dicarboxylic acid with hexamethylenediamine is studied. The kinetic control was carried out by sampling of the reaction medium in time and determination of a quantity of hydrogen chloride obtained as a result of the reaction. Thus, under the action of the chlorohydride group and the aliphatic amino group, HCl is isolated (Voronkov *et al.,* 2004).

It is known from the literature that such reactions proceed in the absence of the catalyst with kinetic equation of the second order (Petruk *et al.,* 2010; Issa *et al.,* 2019).
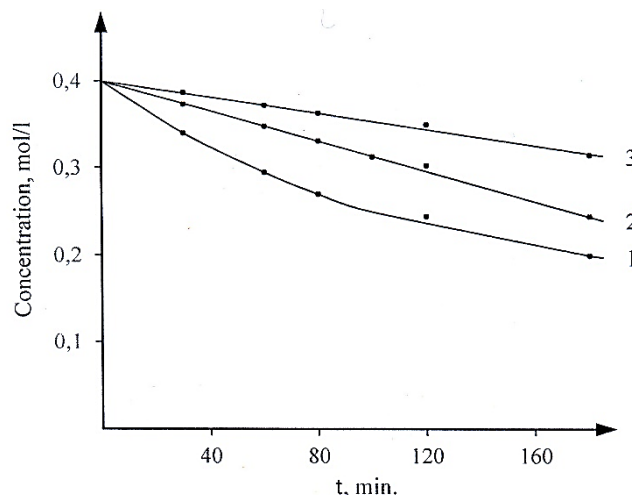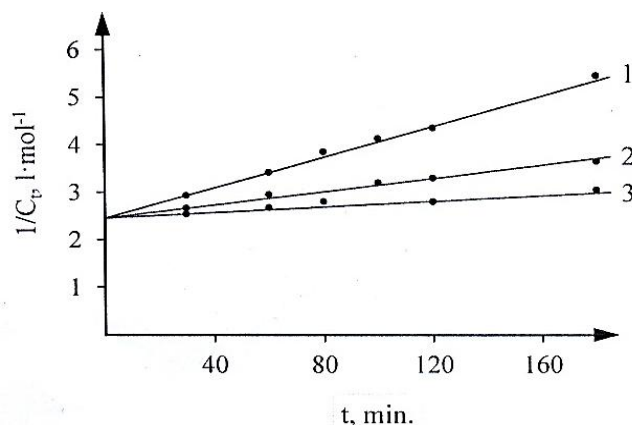
Fig. 2. Curves of dependence of anhydride concentration on time in the polycondensation reaction of dichloroanhydride of bisaccharin-dicarboxylic acid with hexamethylenediamine. $M_1 = M_2 = 0.4$ mol/l. T, K: 313 (1), 303 (2) and 293 (3)

In Fig. 2 the curves of the dependence of the concentration of dichloroanhydride on time at various temperatures in the polycondensation reaction of dichloroanhydride of bisaccharin-dicarboxylic acid with hexamethylenediamine are presented. It can be seen from the presented curves that with temperature rise, the consumption of dichloroanhydride (of course, diamine) is in time accelerated. So, the initial rate values of the polycondensation reaction at 293 K, 303 K and 313 K are $2.91 \cdot 10^{-3}$, $6.03 \cdot 10^{-3}$ and $12.1 \cdot 10^{-3}$ mol/(l·min) (respectively).

The polycondensation reaction of dichloroanhydride of bisaccharin-dicarboxylic acid with diamine is an irreversible process. Of course, it is more likely that the considered reaction is subjected to the kinetic equations of the second order of irreversible (nonequilibrium) polycondensation (Kima *et al.,* 2020). Indeed, the kinetic curves shown in Fig.1 give straight lines in coordinates $1/C_t \sim f(\tau)$). The fraction crossed by these lines from the coordinate axis is equal to $1/C_o$- (C_o- and C_t – initial and t – instantaneous concentrations of dichloroanhydride groups, respectively (Fig.3. and Table 1).

Table 1. Dependence of C_t and $1/C_t$ values on the time in the polycondensation reaction of dichloroanhydride of bisaccharin-dicarboxylic acid with hexamethylenediamine

| T, K	Parameter	Reaction time, min					
		30	60	80	100	120	180
313	$1/C_t$ (C_t)	2.95 (0.34)	3.35 (0.30)	3.70 (0.27)	4.0 (0.25)	4.2 (0.24)	5.2 (0.192)
303	$1/C_t$ (C_t)	2.7 (0.37)	2.95 (0.34)	3.0 (0.33)	3.2 (0.31)	3.3 (0.30)	3.65 (0.27)
293	$1/C_t$ (C_t)	2.6 (0.39)	2.7 (0.37)	2.80 (0.36)	-	2.85 (0.35)	3.1 (0.323)

Figure 3. Dependence of the polycondensation reaction of dichloroanhydride of bisaccharin-dicarboxylic acid with hexamethylenediamine. $1/C_t - f(\tau)$. $M_1 = M_2 = 0.4$ mol/l. T, K: 313 (1), 303 (2) and 293 (3)

According to the values of the angular coefficients of these straight lines, the rate constant values of the polycondensation reaction at various temperatures is found (Table 2.)

Table 2. Some kinetic parameters of the polycondensation reaction of dichloroanhydride of bisaccharin-dicarboxylic acid (M_1) with hexamethylenediamine (M_2)

T, K	M_1, mol/liter	M_2, mol/liter	$W \cdot 10^3$, mol/(liter·min)	$k \cdot 10^2$, mol/(liter·min)	E, kJ/mol
313	0.4	0.4	12.1	7.59	
303	0.4	0.4	6.08	3.80	54.2
293	0.4	0.4	2.91	1.82	

As can be seen from Table, the rate constants values are quite high and are considerably increased (about 4 times) with temperature rise (293÷313K).
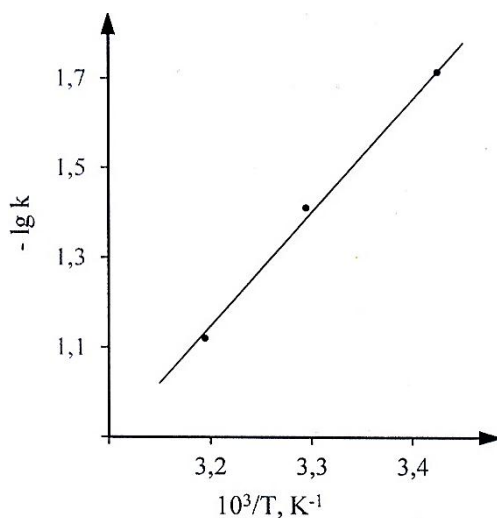
Fig. 4. Dependence of the logarithm of the rate constant of the polycondensation reaction of dichloroanhydride of bisaccharin-dicarboxylic acid with hexamethylenediamine on reverse temperature

In Fig. 4 the temperature dependence of the logarithm of the rate constant of the polycondensation reaction of dichloroanhydride of bisaccharin-dicarboxylic acid with hexamethylenediamine has been shown. This dependence has the form of a straight line, and the activation energy of the polycondensation process is calculated on the angular coefficient value of this line ($E_a = 54$ kCl/mol).

We have also studied the solubility of the synthesized polyamidosulfoimides in various polar solvents (DMFA, DMAA, DMSO, N-methyl pyrrolidone) depending on the structure. The increase of methylene fragments in diamines leads to an increase of the solubility of polymers.

The thermal stability of the synthesized polyamidosulfoimides is studied by the methods of DTA and TGA on the device Q-1500 q. As the investigations showed, 10% polymer mass loss is connected with the solvent residue of the sulphurized polyamidoimide. The rapid mass loss is observed at 653-673K, this has been apparently connected with the active decomposition of SO_2–N bond. In comparison of the thermal stability of the sulphurized polyamidoimide on the basis of ethylenediamine, tetramethylenediamine and hexamethylenediamine, the mass losses in these polymers are relatively comparable (Dolbin *et al.,* 2007).

The polymers containing sulfamide groups are film- and fiber-forming materials and have some advantages in comparison with usual polymers (Zhang *et al.,* 2019). They have better colourability, high resistance to radiation, light and are resistant in relation to acid and alkaline hydrolysis.

The synthesized polyamidosulfimides can be used in electrical engineering, electronic and nuclear industries at higher temperature conditions.

4.   Conclusion

For the first time, the regularities of the polycondensation reaction of dichloroanhydride of bisaccharin-dicarboxylic acid with aliphatic diamines is investigated. The optimal conditions for the synthesis of high-molecular polyamidosulfoimides, possessing improved solubility in aprotic solvents and thermal stability is found.

The regularities of the influence of aliphatic fragments in the initial compounds on the polycondensation process and the properties of the obtained polymer materials is revealed.

The composition, structure and basic properties of the synthesized polymers have been studied by spectroscopic and thermogravimetric methods and elemental analysis.

By methods of thermal analysis (TG, DTA), the kinetic parameters are determined. The optimal conditions and temperature regime of polyamidosulfoimides are found.

The polymers containing sulfamide groups are film- and fiber-forming materials and have some advantages in comparison with usual polymers. They have better colourability, high resistance to radiation, light and are resistant in relation to acid and alkaline hydrolysis.

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