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Synthesis of novel polymers on the basis of polycondensation of diamines with esters of tetracarboxylic acid

Polymerization of heterocyclic monomers is known to lead to the formation of polymers possessing complex of predictable practically useful properties, in particular, thermoplastic and heat-resistant ones. As object of research we used heterocyclic polyamide synthesized by polycondensation of ethyl ester of ethylenetetracarboxylic acid with polyfunctional diamine. For our research the method of low-temperature polycondensation which began to be applied recently was the most suitable method for obtaining polyamides. The advantage of this method is reducing the duration of the polycondensation and the possibility of obtaining products of high molar mass. Low-temperature polycondensation process is also used for obtaining unstable at the melting point polyamides with aromatic nuclei.

Key words: heterocyclic monomers, polycondensation, polyamides, thiazoles, tetracarboxylic acids, polyfunctional diamine.

Despite the impressive progress made in the synthesis of polymers with specific properties a search of new ways of polycondensation, establishing principles of macromolecular design, development of new advanced polymer materials, and in-depth study of their properties is still remained of current interest. Advances in the technology of aromatic polycondensation polymers were reflected in industrial (or semi industrial) manufacture of plastics, fibers and films on their basis, which are widely used in various fields of human activities [1–3].

Each stage of the addition reaction does not depend on previous ones and does not affect the probability of subsequent similar acts of addition. The reactivity of the functional groups is actually independent of the number of units in the polymer homologue. Multifunctional products can only participate in the polycondensation reaction leading to the obtaining of high molar mass polymers. So we mean only those functional groups that under chosen conditions may interact with each other. Presence of two or more functional groups in the starting compound is the necessary condition for the polycondensation reaction.

Linear polymer is known to be formed of bifunctional compounds polycondensation in the absence of by-side reaction. If the starting monomers contain three or more functional groups capable of reacting with each other the number of functional groups in the macromolecule increases with each act of addition, so branched polymer can be formed. Cross-linked polymers are formed at further interaction of branched macromolecules.

Another necessary requirement for the polycondensation reaction is the absence of competing processes leading to decreasing the number of functional groups.

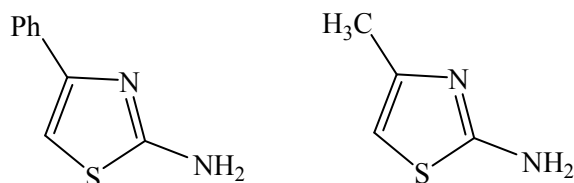
Depending on the stability of the newly forming in polymer functional groups relative to in reaction products of low molar mass and polycondensation conditions the process may be an equilibrium (reversible) and non-equilibrium (irreversible). In those cases where the newly created functional groups can interact with the low-molar-mass reaction product polycondensation is reversible and the equilibrium constant for each act of addition is defined by reaction conditions, and activation energy of the reverse process.

When proceeding polycondensation practically there is no monomer in the reaction medium already at the initial stages, and macromolecular growth occurs as a result of interaction of dimers, trimers, and then oligomers and high molar mass compounds. It was experimentally found that the reactivity of the terminal functional group does not decrease with increasing length of the macromolecules. Thus for the whole process the growth rate constant remains unchanged as well as the activation energy of each stage.

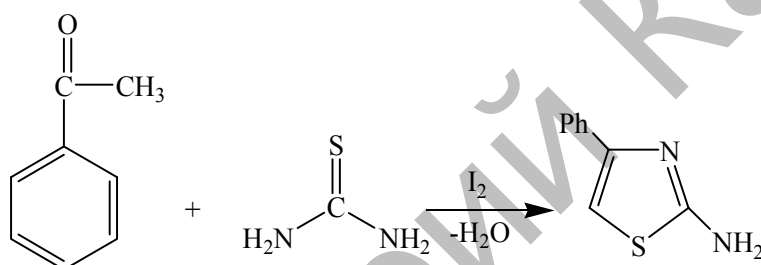
Step-growth polymerization is widely used both in industrial and laboratory synthesis of polymers as well as addition polymerization. Polycondensations were carried out in solid phase, in melt, in solution, in emulsion, on interface, in matrices.

For obtaining high-molar-mass polymers it is necessary to keep equimolar ratio of the reactants, to prevent side reactions of functional groups, polymer thermodestruction, but in the case of equilibrium processes low-molar-mass products must be fully removed from the reaction zone.

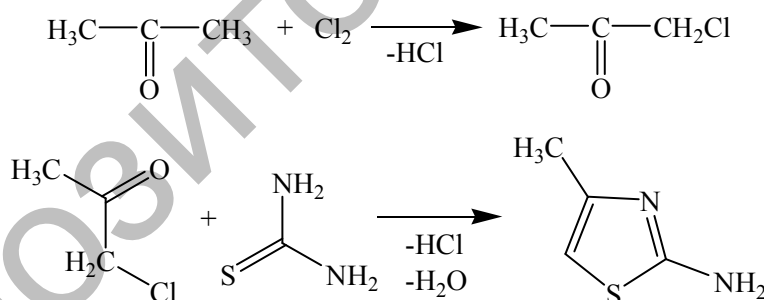
As initial compounds for the synthesis of the starting diamines containing a thiazole moiety, we used 2-amino-4-phenylthiazole (I) and 2-amino-4-methylthiazole (II) synthesized according to Hantzsch reaction scheme which are further successfully condensed with a benzaldehyde in the presence of hydrochloric acid according to the known scheme [4, 5]. Substituents at 4-position do not affect the reaction route and condensation takes place onto the 5-position.



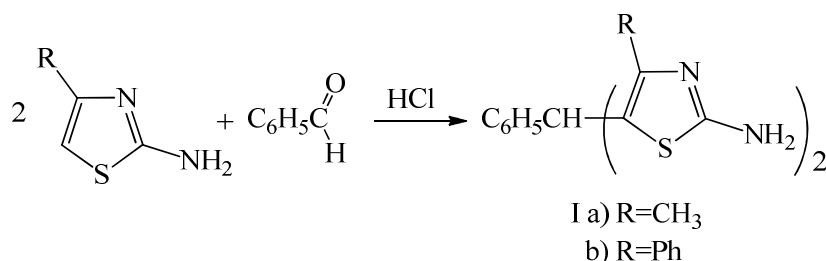
These compounds were obtained by Hantzsch synthesis which is interaction of α -(ketone halides) of aldehydes with thioamides. 2-Amino-4-phenylthiazole was synthesized by interaction of acetophenone with thiourea in the iodine presence.



2-Amino-4-methylthiazole was obtained from chloroacetone and thiourea. For this reaction chloroacetone was previously synthesized by chlorination of acetone according [6].



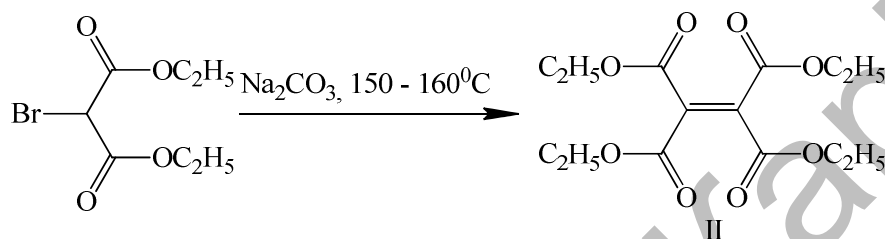
The presence of sulfur in aromatic cycle is equivalent to $-\text{CH}:\text{CH}-$ group that is well illustrated by the close similarity of physical and chemical properties between benzene and thiophenes, or thiazoles and pyridines. The amino group of 2-aminothiazole in the para-position relative to the position 5.



Couple of decades ago tetracarboxylic acids did not find practical application, although a significant number of them have been isolated from the products of oxidation of organic compounds or at identification of diene systems according to Diels–Alder reaction. However, the situation was changed dramatically when it was found that the tetracarboxylic acids and their functional derivatives may be used as starting compounds for the synthesis of thermostable polymers (polyimides), plasticizers, and antioxidants, as hardeners of epoxy resins, etc.

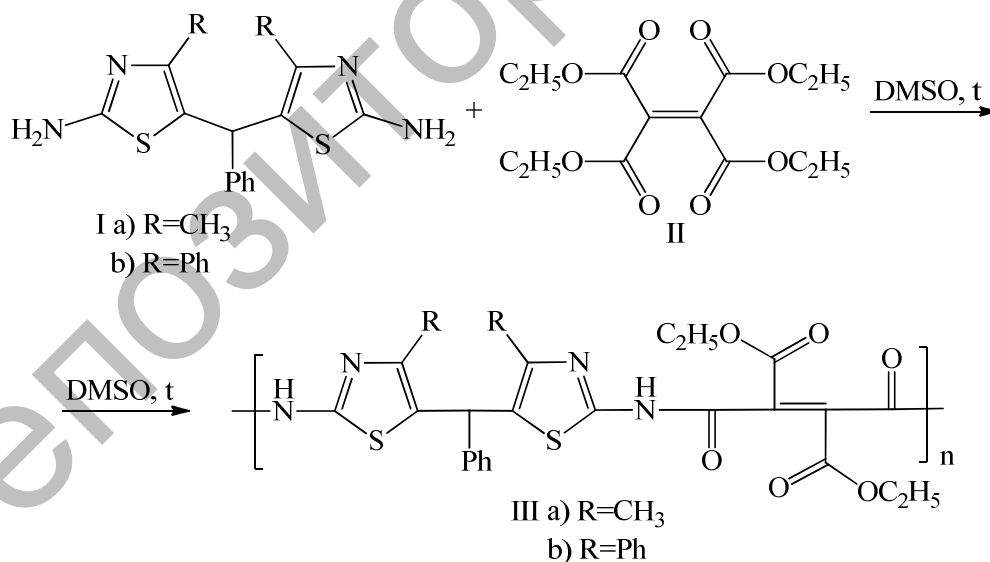
There are the many methods for the synthesis of carboxylic acids but for the preparation of compounds of our interest the following ones such as oxidation of organic compounds, cycloaddition reactions, condensation of dicarboxylic acids and their derivatives and syntheses with malonic ester can be used.

Ethyl ester of ethylenetetracarboxylic acid (II) obtained by heating bromomalonic ester with anhydrous sodium carbonate was chosen as one of the monomers for the polycondensation.



Interest for aromatic dicarboxylic acid chlorides as monomers for the synthesis of condensation polymers is due to the high reactivity in the energy interaction at low temperatures with compounds having active hydrogen atoms (alcohols and amines) in the presence of a proton acceptor. The usual way of carrying out this process called interfacial condensation is based on Shotten–Bauman classic acylation reaction of amines and alcohols and Hinsberg's separation of amines. The reaction occurs at the interface of the solution of dicarboxylic acid chloride in organic solvent and an aqueous solution of a diamine or diol.

The polycondensation of compounds Ia and Ib with the compound II was carried out by high-temperature polycondensation in DMSO according to the scheme:



The IR spectra of the obtained compounds have bands typical for NH- group: (ν , cm^{-1}) 3445 for IIIa; 3438 for IIIb. This indicates the presence of substituent at aminogroup.

Solubility of IIIa, b polyamides was checked in dimethylformamide, dimethylsulfoxide, tetrahydrofuran, concentrated sulfuric acid. These polymers are insoluble in common organic solvents. All polyamides are readily soluble in aprotic polar solvents.

Intrinsic viscosity of IIIa, b polyamides is determined by means of Ubbelohde viscometer at 25°C using a solution of the polymer in DMFA. The intrinsic viscosity is determined by the formula (1):

$$[n] = \frac{2.3}{C} \log \frac{n}{n_0}, \quad (1)$$

where C is concentration of solution 0.5 g/100 ml; n/n_0 is relative viscosity.

Low intrinsic viscosity values polyamides IIIa, b are due to the fact that they are obtained by high temperature polycondensation. In addition, it may be connected with the low reactivity of ethyl ester of ethylenetetra-carboxylic acid, and possible partial decomposition of this compound when exposed to heating.

Experimental part

IR spectra of compounds synthesized were recorded on a spectrometer «Nicolet Avatar-360» using KBr tablets (measurement error is 0.2 cm^{-1}).

Reactions routes and compounds individuality were monitored by TLC on standard plates «Silufol UV-254» in the system of benzene:ethanol = 6:1. Plates were detected with a UV lamp.

Synthesis of di(2-amino-4-methylthiazyl-5)phenylmethane. A mixture of 0.1 mol of 2-amino-4-methylthiazole and 10 ml of concentrated hydrochloric acid was heated up to 100 °C and poured dropwise 0.05 mol of benzaldehyde. The temperature was then raised to 150 °C and mixture was boiled for 4 h. After cooling the reaction mixture was dissolved in water and basified with ammonia solution until slightly alkaline reaction. The precipitate was filtered under a water pump vacuum, dried and reprecipitated from DMF with water. Product yield was 55 %. M_p is 180 °C. IR spectrum, ν , cm^{-1} : 3276 and 3446 (NH_2).

Synthesis of di(2-amino-4-phenylthiazyl-5)phenylmethane. A mixture of 0.1 mol of 2-amino-4-methylthiazole and 10 ml of concentrated hydrochloric acid was heated up to 100 °C and poured dropwise 0.05 mol of benzaldehyde. The temperature was then raised to 150 °C and mixture was boiled for 4 h. After cooling the reaction mixture was dissolved in water and basified with ammonia solution until slightly alkaline reaction. The precipitate was filtered under a water pump vacuum, dried and reprecipitated from DMF with water. Product yield was 75 %, M_p is 221 °C. IR spectrum, ν , cm^{-1} : 3240 and 3434 (NH_2).

Investigation of solubility of ethyl ester of ethylenetetra-carboxylic acid in ethanol. Yield of dried air colorless product which melts at 52.5–53.5 °C is 95–110 g (47–55 % of theoretical value). Distilling off the alcohol from the mother liquor, distilling residue in vacuum and recrystallization of solidified distillate can increase the product yield to 110–115 g (55–57 % of theoretical value).

Table

Solubility of ethyl ester of ethylenetetra-carboxylic acid in 100 ml of 95 % ethyl alcohol

2.0 g	at 0 °C	16.0 g	at 30 °C
2.5 g	at 11 °C	19.0 g	at 31 °C
1.0 g	at 16 °C	28.0 g	at 33 °C
8.0 g	at 23 °C	35.0 g	at 34 °C
9.7 g	at 26 °C	61.0 g	at 36,5 °C

Synthesis of polyamides IIIa, b. 1 mmol of the diamine and 1 mmol of ethyl ester of ethylenetetra-carboxylic acid were dissolved in dry DMSO and heated with rapid stirring for 10 hours. Then after cooling mixture was poured into 30 ml of distilled water, the precipitated polymer was filtered and dried. Yields of polyamides IIIa, b are 64 and 68 %, respectively. IR spectrum, ν , cm^{-1} : 3445 (NH) for IVa; 3438 (NH) for IIIb.

References

- 1 Соколов Л.Б. Основы синтеза полимеров методом поликонденсации. — М.: Химия, 1979. — С. 245–300.
- 2 Monticelli O., Russo S., Campagna R., Voit B. Preparation and characterization of blends based on polyamide 6 and hyperbranched aramids as palladium nanoparticle supports // Polymer. — 2005. — Vol. 46. — P. 3597–4606.
- 3 Коршак В.В. Катализ в реакциях поликонденсации // Успехи химии. — 1982. — Т. 51, № 12. — С. 2096–2109.
- 4 Turchi I.J., Dewar J.S. Progress in thiazole chemistry // Chem. Rev. — 1975. — Vol. 75, № 5. — P. 389.
- 5 Розенцвейг Г.Н., Розенцвейг И.Б., Левковская Г.Г., Мирскова А.Н. Синтез замещенных 4-(N-арилсульфонил)амино-тиазолов из N-(1-тиоацетиамидо-2,2-дихлор-2-фенилэтиларенсульфонамидов) // Журнал орг. хим. — 2003. — Т. 39, № 12. — С. 1875–1876.
- 6 Albertson N.F. Amination reaction in thiazoles derivatives // J. Am. Chem. Soc. — 1989. — Vol. 70, № 6. — P. 669.

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Диаминдердің тетракарбон қышқылдарының эфирлерімен поликонденсация реакциясы негізінде жаңа полимерлер синтезі

Гетероциклды мономерлер практикалық, соның ішінде жылуға төзімді және жылу пластикалық пайдалы болжамды қасиеттері бар, комплексті полимерлердің түзілуіне әкелетіні белгілі. Зерттеу нысанымыз ретінде этилентетракарбон қышқылының этил эфирінің полифункционалды диаминмен поликонденсациясымен синтездеп алынған гетероциклды полиамид қолданылды. Біздің зерттеулерге полиамидтерді алу үшін аса ыңғайлы әдіс ретінде төменгі температуралық поликонденсация әдісі таңдалды. Бұл әдістің ерекшелігі — поликонденсация ұзақтығының азаюы және жоғарғы молекулалық массамен заттар алу мүмкіндігінде. Сонымен қатар төменгі температуралық поликонденсация процесі балқу температурасы кезінде тұрақты емес ароматикалық ядроларымен полиамидтерді алу үшін пайдаланды.

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Синтез новых полимеров на основе реакции поликонденсации диаминов с эфирами тетракарбоновой кислоты

Известно, что гетероциклические мономеры приводят к образованию полимеров с комплексом прогнозируемых практически полезных свойств, в частности, термостойких и термопластичных. В качестве объекта исследования нами использован гетероциклический полиамид, синтезированный поликонденсацией этилового эфира этилентетракарбоновой кислоты с полифункциональным диамином. Наиболее подходящим методом получения полиамидов в ходе наших исследований оказался метод низкотемпературной поликонденсации, который начал применяться сравнительно недавно. Преимуществом этого метода является уменьшение длительности поликонденсации и возможность получения продуктов с высокой молекулярной массой. Процесс низкотемпературной поликонденсации также используют для получения нестабильных при температуре плавления полиамидов с ароматическими ядрами.

References

- 1 Sokolov L.B. *Fundamentals of polymer synthesis by polycondensation*, Moscow: Khimiya, 1979, 563 p.
- 2 Monticelli O., Russo S., Campagna R., Voit B. *Polymer*, 2005, 46, p. 3597–4606.
- 3 Korshak V.V. *Rus. Chem. Rev.*, 1982, 51, 12, p. 2096–2109.
- 4 Turchi I.J., Dewar J.S. *Chem. Rev.*, 1975, 75, 5, p. 389.
- 5 Rosenzweig G.N., Rosenzweig I.B., Levkovskaya G.G., Mirskova A.N. *J. Org. Chem.*, 2003, 39, 12, p. 1875–1876.
- 6 Albertson N.F. *J. Am. Chem. Soc.*, 1989, 70, 6, p. 669.

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