

# Synthesis of Aromatic Diamines of the Pyrimidine Series and Their Use for Creating New Prospective Polymeric Materials

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## Abstract

Alternative methods of the synthesis of pyrimidine containing diamines, initial monomers for obtaining heat-resistant high module polymers (polyimides) used in creation of prospective materials for technical innovations are considered. According to the structure of diamines the methods of their synthesis are systematized, an estimation of their reactivity is presented. The questions concerning technological rationality, availability of initial raw material and the possibility of process scaling at separate synthetic stages are examined. Data are presented on thermal stability and deformation strength characteristics of pyrimidine-containing polyimides promising for the creation of materials operating within a wide range of extreme thermal conditions in a number of modern engineering fields.

**Key words:** aminophenyl pyrimidines, pyrimidine-containing polyimides, films, fibres, thermal stability, strength properties

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## INTRODUCTION

The derivatives of six-membered nitrogen containing heterocycles such as pyridine, pyrimidine and other azines, find extensive application in medicine, agriculture, in various fields of engineering and scientific research. Among them a highly important place is occupied by the derivatives with aryl and hetaryl substituents those exhibit biological activity, as well as complexation, photochromic, optical, liquid-crystal and other properties.

One of prospective scopes of aryl-substituted nitrogen-containing heterocyclic compounds application as initial components for obtaining heat-resistant polymeric materials, heat and light stabilizers is presented by the chemistry of polymers. Heat-resistant polymeric materials are used in various branches of modern engineering, and the requirements for their functional parameters are constantly increased. Aromatic polyimides (or polyarimides) exhibit the highest thermal stability and a complex of other valuable technical properties among all the polymeric organic materials existing nowadays [1, 2]. High thermal

stability, radiation resistance, good deformation strength characteristics and dielectric properties inherent in polyarimides of the benzene series are connected with the features of their chemical structure. In particular, this could be caused by the fact that there are alternating aromatic and imide cycles in the basic chain with chemical inertness and thermal stability inherent in them owing to the symmetry and strong intermolecular interaction between polymeric chains [1–3]. Increasing the requirements for polymeric materials from the direction of modern engineering, in particular concerning the thermal stability and strength properties, stimulate searching for new ways to improve these parameters. One the ways consists in introducing heterocyclic fragments into the basic polyimide chain [4–7].

The studies in this field within last two decades performed at the Institute of Macromolecular Compounds, RAS (St. Petersburg), together with the Novosibirsk Institute of Organic Chemistry, SB RAS (Novosibirsk), have allowed the researchers to obtain a large series of polyimides based on pyrimidine containing diamines synthesized according specially developed techniques as well as to create a number of polyimide materials (films and fibres) with high thermal stability parameters and good strength characteristics as compared to other organic polymers. It has been demonstrated that bis(aminophenyl)pyrimidines interacting with dianhydrides of aromatic tetracarboxylic acids are capable to form polymeric molecules consisting of polyamido acids (PAA) those are transformed into high molecular weight polyimides after chemical or thermal imidization. Some of the polyimides obtained surpass the best Russian and foreign analogues in strength properties and thermal stability, which allows one to attribute the bis(aminophenyl)pyrimidines to monomers those could be successfully used in the creation of highly efficient polyimide materials with a wide range of applications. In the development of the methods for the synthesis of such monomers an important attention is focused not only on the technological rationality, availability of initial raw material and the opportunity of scaling the chemical processes at certain synthetic stages, but also on minimizing the amount of waste products at a great production volume.

#### METHODS FOR THE SYNTHESIS OF PYRIMIDINE-CONTAINING DIAMINES

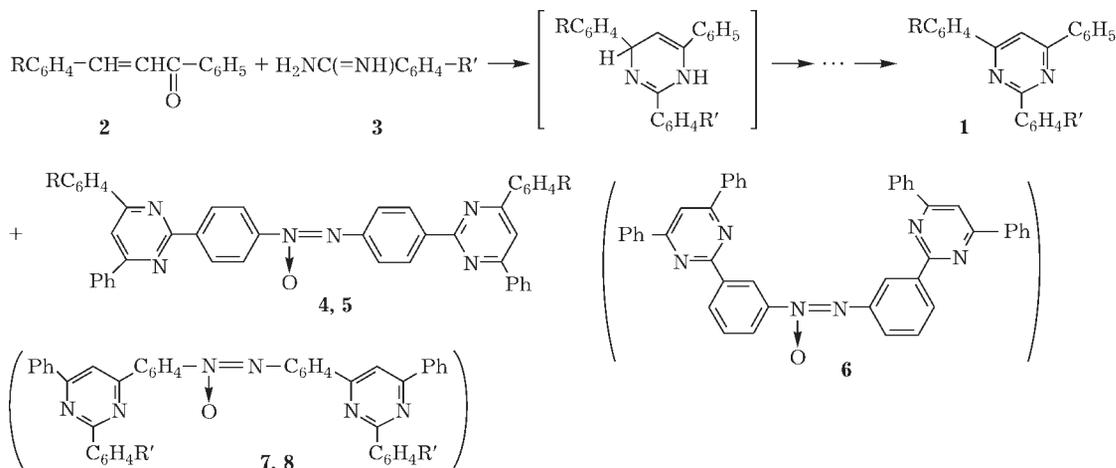
In the synthesis of aryl pyrimidines with various arrangement and number of substituted phenyl groups in the pyrimidine cycle one uses to involve well-known general approaches those include the condensation of  $\alpha,\beta$ -unsaturated carbonyl compounds of the benzene series,  $\beta$ -dicarbonyl compounds or their latent forms with formamide, amidines, guanidines, ureas or thioureas. Historically, diamino derivatives of 2,4,6-triaryl pyrimidines, being most synthetically available compounds, first of all have drawn attention of researchers in the field of polymeric chemistry as possible monomers with polynuclear aromatic structure in the reaction of polycondensation.

Further some synthetic windfalls found in the development of alternative methods for the synthesis of these triaryl pyrimidines have been transferred to the other, less structurally loaded diamines of pyrimidine series. Keeping the historically developed chronology of performed studies on the synthesis of such diamines and on using them for obtaining new polymers, the present review is devoted to discussing various aspects of chemical transformations, from diamino substituted triaryl pyrimidines, with the further transition to diamines and amines in the series of diaryl pyrimidine.

#### *Amino substituted 2,4,6-triaryl pyrimidines*

Usually 2,4,6-triaryl derivatives of pyrimidine **1** (Scheme 1) are formed through the interaction between aryldene acetophenones **2** and arylamidines **3**. As initial substances one can use both aromatic halogen substituted compounds [8, 9], and more available nitro containing analogues [10, 11]. However, when nitro substituted benzamidines and chalcones are used with the reaction carried out in boiling ethanol medium in the presence of alkali, the formation of by-products such as azoxyaryl pyrimidines **4–8** is observed, which results in a considerable reduction of the yield values for nitrophenyl pyrimidines [10].

The formation of azoxy compounds **4–8** could be presented as a result of interconnected processes of the dihydropyrimidine cycle



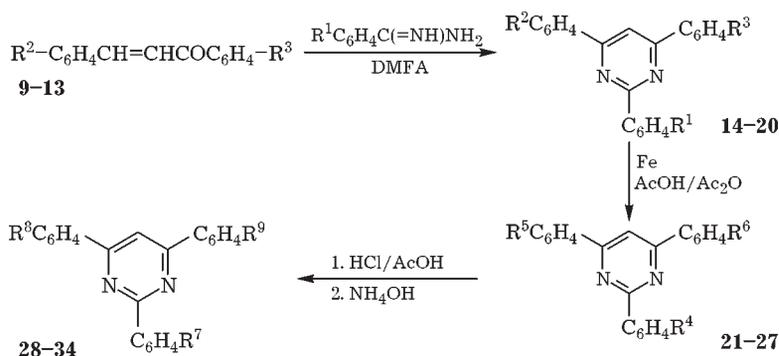
R = H (1, 2, 4); *p*-Br (1, 2, 5); *p*-NO<sub>2</sub> (1, 2); R' = H (1, 3, 7); *p*-Br (1, 3, 8); *m*-NO<sub>2</sub> (1, 3); *p*-NO<sub>2</sub> (1, 3)

Scheme 1.

oxidation and the nitro group reduction to give the azoxy group in transient dihydropyrimidines formed. It has been demonstrated that the reaction carrying out at a higher temperature (120–130 °C) and the use of amidine excess in quality as a basic catalyst allows one to quench the formation of azoxy compounds due to the fact that the reaction rate for nitrophenyldihydropyrimidine dehydration by atmospheric oxygen exceeds is higher than the dehydration rate for the latter due to the nitro groups themselves [11]. Under these conditions the interaction between nitro substituted chalcones **9–13** and benzamidines proceeds smoothly enough resulting in the formation of bis(nitrophenyl)

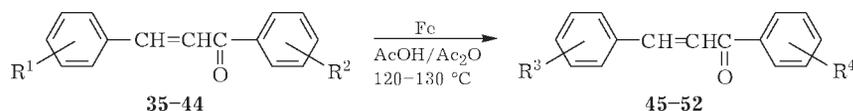
pyrimidines **14–20** with the yield within the range of 40–66 % (Scheme 2). The sole exception is provided by the reaction between dinitrochalcone **10** with benzamidine accompanied with a profound resinification.

In some cases the transformation of pyrimidine dinitro derivatives into diamino derivatives should be carried out in two stages with the use of the reactions of reductive acetylation and the subsequent acidic hydrolysis of pyrimidine acetyl amino derivatives obtained. The choice of such method is based on the fact that the obtaining of acetyl derivatives and the subsequent hydrolysis resulting in the formation of amine derivatives proceed with a high



R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>: *p*-NO<sub>2</sub>, *p*-NO<sub>2</sub>, H (**9**, **14**); H, *p*-NO<sub>2</sub>, *p*-NO<sub>2</sub> (**10**, **15**); *m*-NO<sub>2</sub>, *m*-NO<sub>2</sub>, H (**11**, **16**); H, *m*-NO<sub>2</sub>, *m*-NO<sub>2</sub> (**12**, **17**); H, *p*-NO<sub>2</sub>, *m*-NO<sub>2</sub> (**13**, **18**); *p*-NO<sub>2</sub>, *m*-NO<sub>2</sub>, H (**11**, **19**); *m*-NO<sub>2</sub>, *p*-NO<sub>2</sub>, H (**9**, **20**); R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>: *p*-AcNH, *p*-AcNH, H (**21**); H, *p*-AcNH, *p*-AcNH (**22**), *m*-AcNH, *m*-AcNH, H (**23**); H, *m*-AcNH, *m*-AcNH (**24**); H, *p*-AcNH, *m*-AcNH (**25**); *p*-AcNH, *m*-AcNH, H (**26**); *m*-AcNH, *p*-AcNH, H (**27**); R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>: *p*-NH<sub>2</sub>, *p*-NH<sub>2</sub>, H (**28**); H, *p*-NH<sub>2</sub>, *p*-NH<sub>2</sub> (**29**); *m*-NH<sub>2</sub>, *m*-NH<sub>2</sub>, H (**30**); H, *m*-NH<sub>2</sub>, *m*-NH<sub>2</sub> (**31**); H, *p*-NH<sub>2</sub>, *m*-NH<sub>2</sub> (**32**); *p*-NH<sub>2</sub>, *m*-NH<sub>2</sub>, H (**33**); *m*-NH<sub>2</sub>, *p*-NH<sub>2</sub>, H (**34**).

Scheme 2.



$\text{R}^1, \text{R}^2$ : *p*-NO<sub>2</sub>, H (**35**); H, *p*-NO<sub>2</sub> (**36**); *p*-NO<sub>2</sub>, *p*-Br (**37**); *p*-NO<sub>2</sub>, *p*-AcNH (**38**); *p*-NO<sub>2</sub>, *p*-NO<sub>2</sub> (**39**); *m*-NO<sub>2</sub>, H (**40**); *m*-NO<sub>2</sub>, *m*-AcNH (**41**); *m*-NO<sub>2</sub>, *m*-NO<sub>2</sub> (**42**); *m*-NO<sub>2</sub>, *p*-NO<sub>2</sub> (**43**); 4'-nitro-3-azachalcone (**44**);  $\text{R}^3, \text{R}^4$ : *p*-AcNH, H (**45**); H, *p*-AcNH (**46**); *p*-AcNH, *p*-Br (**47**); *p*-AcNH, *p*-AcNH (**48**); *m*-AcNH, H (**49**); *m*-AcNH, *m*-AcNH (**50**); *m*-AcNH, *p*-AcNH (**51**); 4'-acetylamino-3-azachalcone (**52**).

Ac = CH<sub>3</sub>CO.

Scheme 3.

yield being not accompanied by the formation of any by-products [10]. Thus it should be noted that the most rational and practically feasible method for the reduction of nitro compounds consisting in the catalytic hydrogenation with hydrogen, in the case of bis(nitrophenyl)pyrimidines sometimes occurs with the formation of a considerable amount of a hard to separate impurity of azo compounds those worsen the quality of target diamines [12]. Bis(acetylamimophenyl)pyrimidines **21–27** have been obtained from corresponding bis(nitrophenyl)pyrimidines **14–20** through the reduction by Fe powder in the mixture of acetic acid and acetic anhydride at 130 °C with the yield of 72–93 % (see Scheme 2) [11].

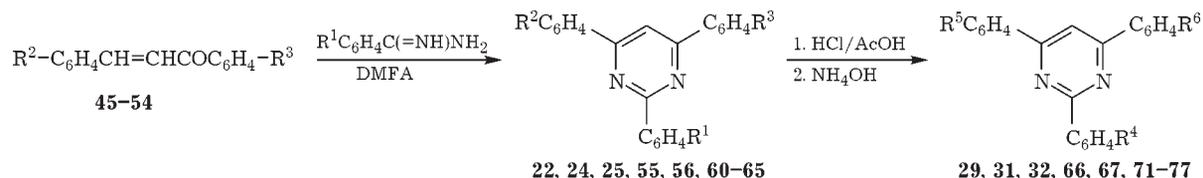
The hydrolytic detachment of the acetyl groups in compounds **21–27** was carried out on heating in the mixture of hydrochloric and acetic acids and the subsequent treatment of the reaction products with an aqueous solution of ammonia. As a result the target an bis(aminophenyl)pyrimidines **28–34** were obtained with the yield of 71–95 % (see Scheme 2) [11].

An alternative method for obtaining amino substituted 2,4,6-triaryl pyridines consists in the use of acetylamino chalcones instead of nitro-

chalcones in the reaction with arylamidines. The initial acetylamino chalcones were obtained directly from nitrochalcones through the reduction by iron in acetic acid in the presence of acetic anhydride [13] (Scheme 3).

The reductive acetylation of nitrochalcones proceeds with the yield of 80–100 % both for *meta*- nitro derivatives, and for *para*-nitro derivatives, therewith in the case of bromonitrochalcone **37** no dehalogenation is observed. Species 4'-nitro-3-azachalcone **44** that contains in the structure the β-pyridyl group in a similar manner results in the formation of the expected 4'-acetylamino-3-azachalcone **52**. To all appearance, no difficulties should also arise in the case of the reductive acylation of isomeric analogues, such as 4'-nitro-2-azachalcone **53** and 4'-nitro-4-azachalcone **54** obtained by means of the condensation of α- and β-pyridinealdehydes with (*p*-acetylamino) acetophenone [13].

Using the condensation of acetylamino chalcones **45–54** with arylamidines the authors of [13] obtained acetylamino phenyl pyrimidines **22, 24, 25, 55, 56, 60–65** with the yield ranging within 48–90 % carrying out the reaction in anhydrous DMFA in the presence of zeolites under air bubbling (Scheme 4).

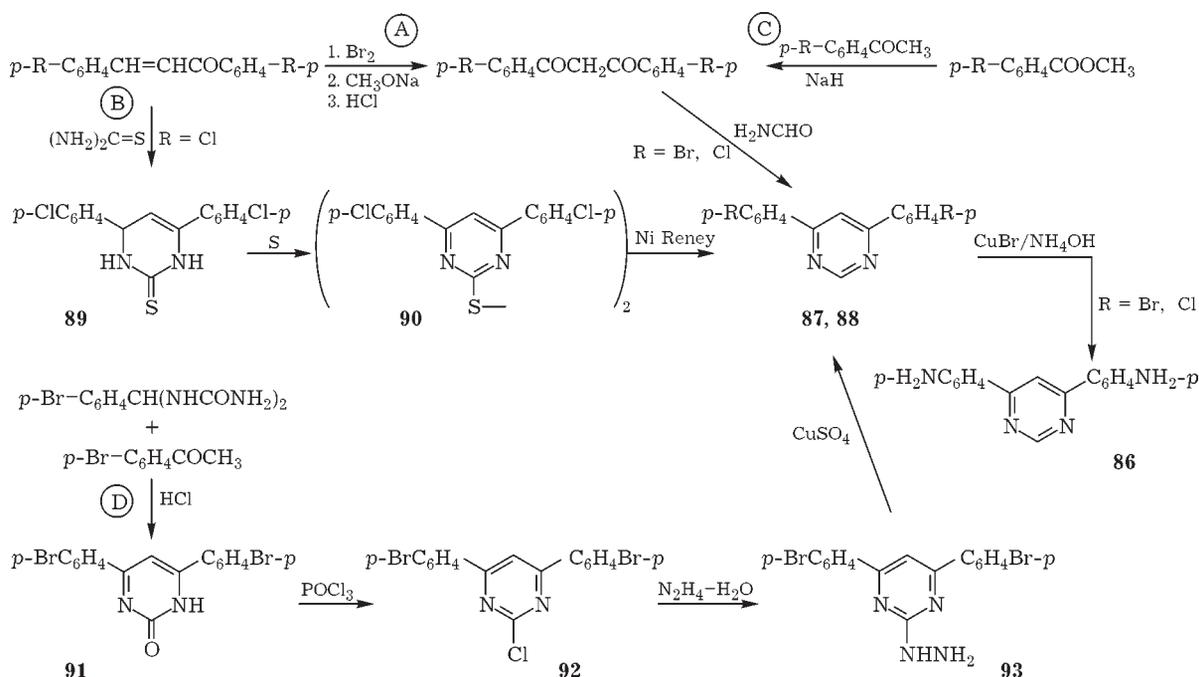


$\text{R}^1, \text{R}^2, \text{R}^3$ : H, NHAc-*p*, NHAc-*p* (**22**); H, NHAc-*m*, NHAc-*m* (**24**); H, NHAc-*m*, NHAc-*p* (**25**); H, NHAc-*p*, H (**55**); H, NHAc-*p*, Br-*p* (**56**); Br-*p*, NHAc-*p*, NHAc-*p* (**60**); NO<sub>2</sub>-*p*, NHAc-*p*, NHAc-*p* (**61**); 4-aza, NHAc-*p*, NHAc-*p* (**62**); Br-*p*, NHAc-*p*, 4-aza (**63**); Br-*p*, NHAc-*p*, 3-aza (**64**); Br-*p*, NHAc-*p*, 2-aza (**65**).

$\text{R}^4, \text{R}^5, \text{R}^6$ : H, NH<sub>2</sub>-*p*, NH<sub>2</sub>-*p* (**29**); H, NH<sub>2</sub>-*m*, NH<sub>2</sub>-*m* (**31**); H, NH<sub>2</sub>-*m*, NH<sub>2</sub>-*p* (**32**); H, NH<sub>2</sub>-*p*, H (**66**); H, NH<sub>2</sub>-*p*, Br-*p* (**67**); Br-*p*, NH<sub>2</sub>-*p*, NH<sub>2</sub>-*p* (**71**); NH<sub>2</sub>-*p*, NH<sub>2</sub>-*p*, NH<sub>2</sub>-*p* (**72**); NO<sub>2</sub>-*p*, NH<sub>2</sub>-*p*, NH<sub>2</sub>-*p* (**73**); 4-aza, NH<sub>2</sub>-*p*, NH<sub>2</sub>-*p* (**74**); NH<sub>2</sub>-*p*, NH<sub>2</sub>-*p*, 4-aza (**75**); NH<sub>2</sub>-*p*, NH<sub>2</sub>-*p*, 3-aza (**76**); NH<sub>2</sub>-*p*, NH<sub>2</sub>-*p*, 2-aza (**77**).

Scheme 4.



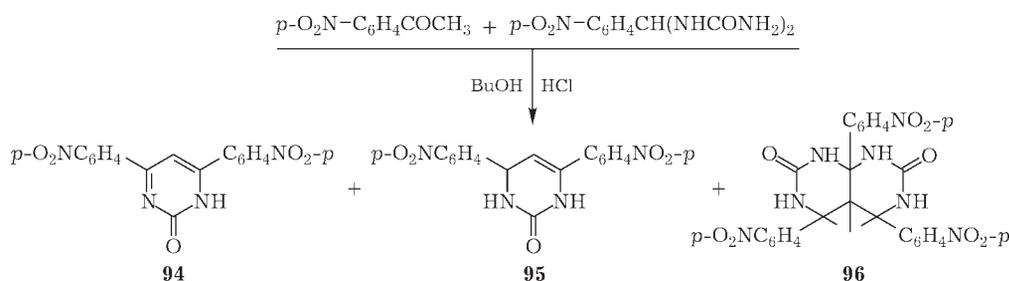


Scheme 6.

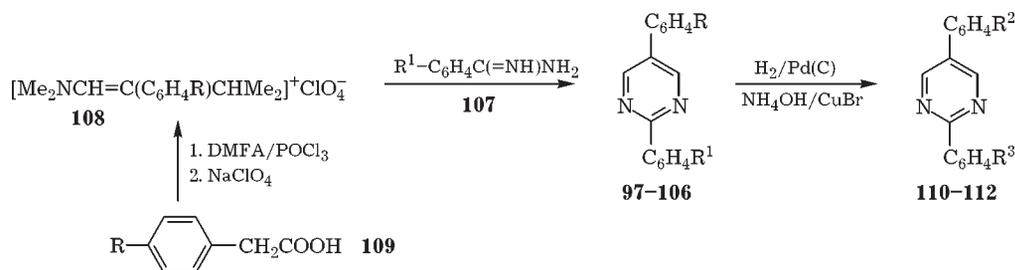
action of 4,6-bis(*p*-bromo- or chlorophenyl)pyrimidines **87** and **88**. It has been demonstrated that the most efficient variant of the synthesis consists in the interaction between formamide and 1,3-bis(*p*-halogenophenyl)propane-1,3-diones formed from 4,4'-dihalogenochalcone (Scheme 6, pathway A) [17]. The pathways of the synthesis B–D presented in Scheme 6 appeared non-efficient from the standpoint of technology and difficult for scaling. The disadvantage of the pathway B consists in the necessity of the dehydration of dihydropyrimidine-2-thione **89** and the subsequent desulphurization of pyrimidine-2-thione **90** via the action of a nickel catalyst. The pathway C is inconvenient because of sodium hydride used in the reaction of condensation. The pathway D requires for using POCl<sub>3</sub> for the transformation of pyrimidine-2-one **91** into corresponding 2-chloro deriva-

tive **92**. As a result of this the reaction with hydrazine hydrate yields 2-hydrazine derivative **93** that gives 4,6-bis(*p*-bromophenyl)pyrimidine **87** with a low yield (see Scheme 6).

The synthesis of the nitro analogue of halogen substituted derivatives **87**, **88** (R = *p*-NO<sub>2</sub>) and its subsequent hydrogenation to yield the target diamine **86** (see Scheme 6, pathway D) appeared also non-efficient since the condensation of *p*-nitroacetophenone with *p*-nitrobenzylidene bisurea results in the formation of a hard to separate a mixture of 2-oxo-4,6-bis(*p*-nitrophenyl)dihydropyrimidine **94**, 2-oxo-4,6-bis(*p*-nitrophenyl)tetrahydropyrimidine **95** and 2,7-dioxo-4,5,8'-tris-(*p*-nitrophenyl)decahydropyrimido[4,5-d]pyrimidine **96**. The prevailing products of this mixture are compounds **95** and **96**, whereas the content of the required product **94** is low (Scheme 7).



Scheme 7.



R: H, *p*-Br, *p*-Cl, *p*-NO<sub>2</sub> (**97-106**, **108**, **109**); R<sup>1</sup>: H, *p*-Br, *p*-Cl, *p*-NO<sub>2</sub>, *m*-NO<sub>2</sub> (**97-107**); R<sup>2</sup>, R<sup>3</sup>: *p*-NH<sub>2</sub>, *p*-NH<sub>2</sub> (**110**); H, *p*-NH<sub>2</sub> (**111**); *p*-NH<sub>2</sub>, H (**112**).

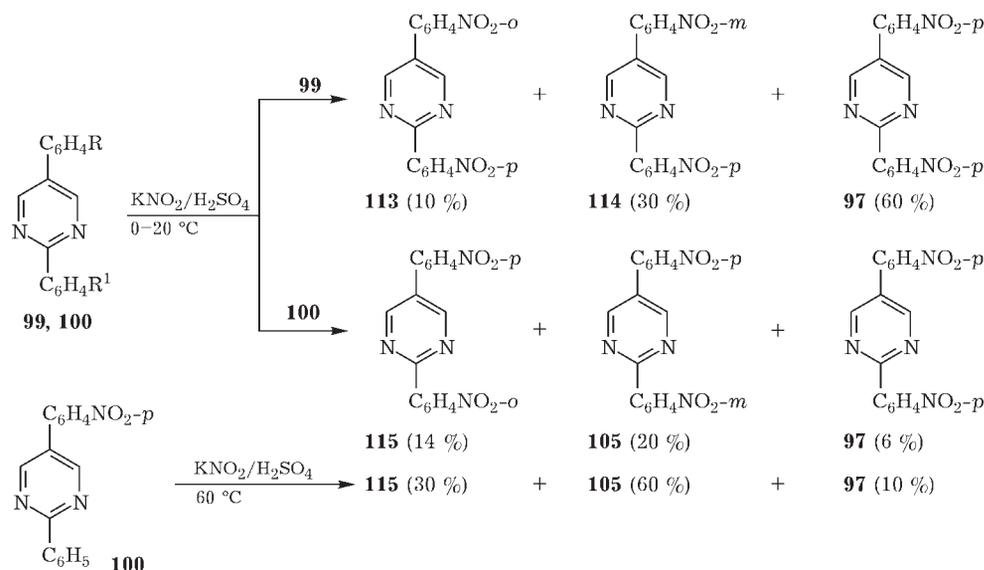
Scheme 8.

The obtaining of the mentioned above nitro analogue was also not gained following the pathway A since bromine did not added to the ethylene bond in 4,4'-dinitrochalkone. The ammonolysis of bis(bromophenyl)pyrimidine **87** (R = *p*-Br) at 160 °C (24 h) in the presence of CuBr using aqueous ammonia results in the formation of the target diamine **86** with the yield of 80 % [17]. In the case of chloro analogue **88** (R = *p*-Cl) under the aforementioned conditions an incomplete substitution of the chlorine by the amino group is observed so that even with the increase in the process duration and growing the temperatures of heating a complete substitution of the chlorine atom is failed [17]. As it follows from the comparison of diamine **86** synthesis pathways under consideration, the most plausible variant is represented by pathway A (see Scheme 6).

#### Amino substituted 2,5-diaryl pyrimidines

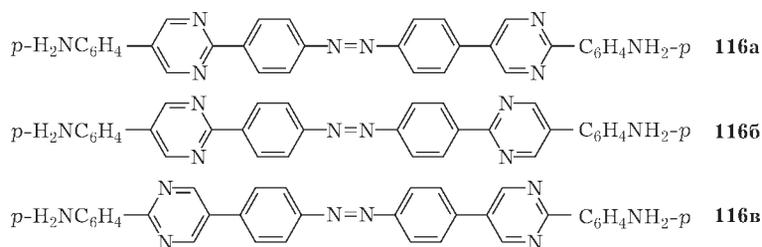
2,5-Diaryl pyrimidines **97-106** with the chloro, bromo or nitro groups in the phenyl rings were obtained with the yields ranging within 83-99 % through the condensation of arylamidines **107** with trimethinium salts **108** those are readily formed from arylacetic acids **109** [18] (Scheme 8).

The studies on the possibilities of obtaining dinitro derivative **97** (R, R<sup>1</sup> = *p*-NO<sub>2</sub>) by means through the nitration of nitrophenyl pyrimidines **99** (R = H, R<sup>1</sup> = *p*-NO<sub>2</sub>) and **100** (R = *p*-NO<sub>2</sub>, R<sup>1</sup> = H) by potassium nitrate in sulphuric acid have demonstrated that irrespective of the temperature of the reaction the nitronium cation attacks all the free positions of the unsubstituted 2- or 5-phenyl groups of compounds **99** and **100** resulting in the formation of the mixture of isomeric 2,5-bis(nitrophenyl)pyrimidines



R, R<sup>1</sup>: H, *p*-NO<sub>2</sub> (**99**); *p*-NO<sub>2</sub>, H (**100**).

Scheme 9.



Scheme 10.

(Scheme 9). Thereof such a way to obtain dinitro derivative **97** is considered to be inefficient.

It has been demonstrated earlier that for the synthesis of dinitro derivative **97** suitable for technological application it is most efficient to use benzyl cyanide (being a large-scale product of the general organic synthesis) as an initial product [19]. The modification of the processes carried out at the stages of obtaining *p*-nitrophenylacetic acid from benzyl cyanide, trimethinium salt **108** ( $R = p\text{-NO}_2$ ) and diaryl pyrimidine **97** [15, 20], has allowed the authors to increase the total yield and to improve the qualitative characteristics of this product. The catalytic hydrogenation of dinitro derivative **97** in DMFA by hydrogen under a pressure of 10 atm results in the obtaining of target diamine **110** with the yield of 95 % [12]. It has been established that isomeric azo compounds **116 a–c** can be formed in insignificant amounts during the hydrogenation process (Scheme 10).

However, carefully matching the conditions for hydrogenation and purification of the reduction product obtained one could obtain diamine **110** with no impurity of azo compounds suitable for the synthesis of polymers [12].

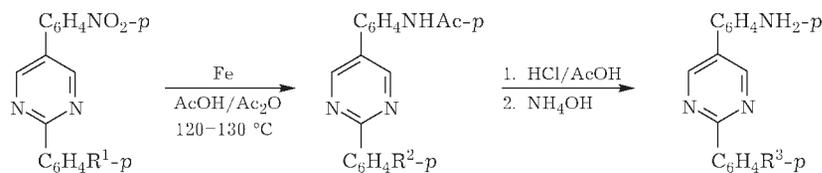
It has been also demonstrated that in order to obtain mono- and bis(aminophenyl)pyrimidines from corresponding nitro substituted 2,5-diaryl pyrimidines a method of reductive acetylation could be successfully applied developed for nitrochalcones and for the synthesis of

aforementioned amino substituted 2,4,6-triaryl pyrimidines [11, 13] (Scheme 11).

Owing to the availability of (*p*-nitrophenyl)pyrimidine **97**, to the high yield and the absence hard-to-scavenge impurities in the obtained acetyl amino substituted pyrimidine **118**, this method can be successfully applied in the laboratory practice for the obtaining of diamine **110** and other similar derivatives, for example amines **111** and **112**.

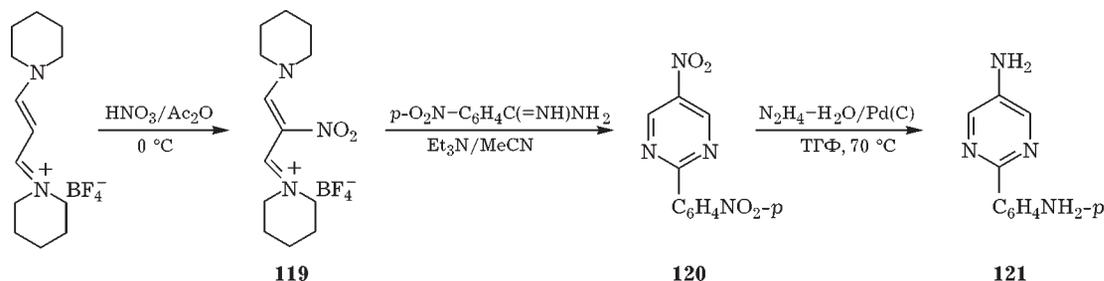
The obtaining of aminodiphenyl pyrimidines through ammonolysis of halogen substituted 2,5-diaryl pyrimidines proceeds in a smooth manner only for bromophenyl substituted species (160 °C, 20 h, CuBr) [18]. In the case of chloro analogues the substitution of chlorine by the amino group could be carried out only for 2-(*p*-chloro)-5-phenyl pyrimidine **101** under much more severe conditions (200 °C, 60 h, CuBr). In the case of 5-chlorophenyl analogue **102** the complete substitution of chlorine by the amino group is failed even under such severe conditions of amination [18] whereupon this method for the obtaining of diamine **110** is rather problematic.

Basing on the data obtained one could conclude that the most plausible method for the synthesis of 2,5-bis(*p*-aminophenyl)pyrimidine **110** consists in the obtaining of 2,5-bis(*p*-nitrophenyl)pyrimidine **97** as a precursor and its catalytic hydrogenation. The examination of this scheme under the conditions of scaling at

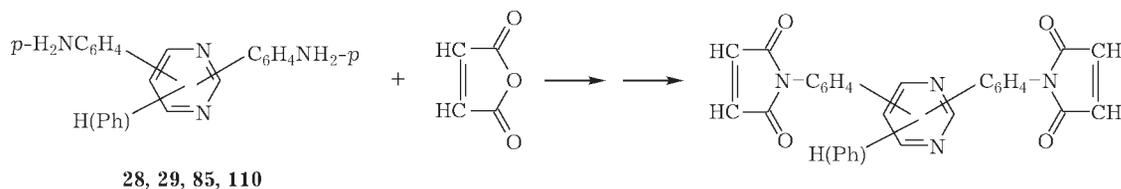


$R^1$ : H (**100**),  $\text{NO}_2\text{-}p$  (**97**);  $R^2$ : H (**117**),  $\text{NHAc}$  (**118**);  $R^3$ : H (**112**),  $\text{NH}_2$  (**110**).

Scheme 11.



Scheme 12.



Scheme 13.

all the chemical stages has demonstrated it to be technologically efficient for the diamine manufacture using pilot installations.

Recently a communication by Chinese researchers has appeared [21] concerning the synthesis of diamine **121** resembling diamine **110** in structure, but containing in the structure only two aromatic rings, the pyrimidine ring and the benzene ring. The synthesis of this compound is based on the condensation of *p*-nitrobenzamidine and nitrotrimethinium salt **119** (Scheme 12).

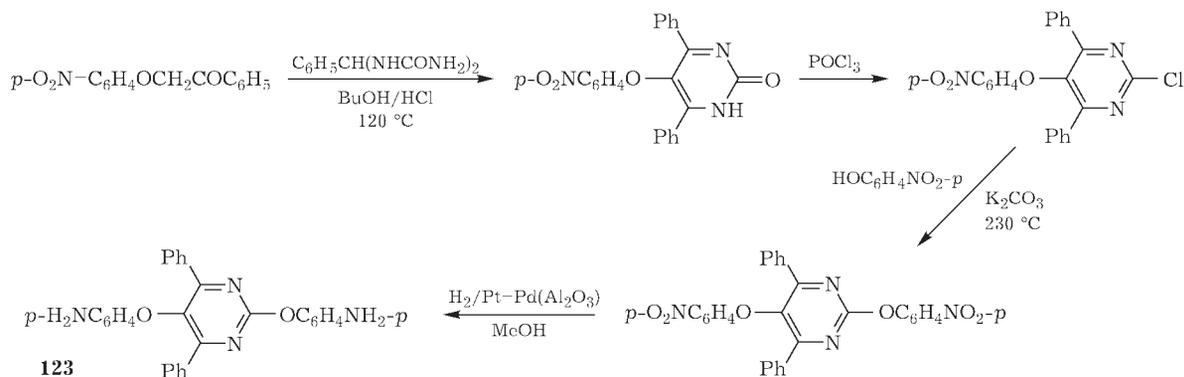
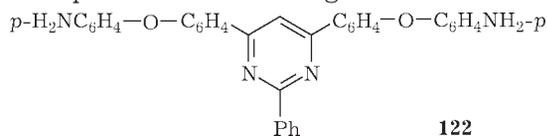
The catalytic reduction of dinitro derivative **120** using the reaction with hydrazine hydrate in the medium of boiling THF results in the formation of the target product with the yield amounting to 92% [21].

Polyimides obtained basing on diamine **121** exhibit high thermal stability and strength values, close to those for polyimides on the base of diamine **110** [21–23].

Bis(aminophenyl)pyrimidines **28**, **29**, **85** and **110** were used also for the obtaining of *N,N'*-bismaleimides (Scheme 13) those are capable to add amines at multiple C=C bond and to undergo polymerization with the formation of tailored three-dimensional structures with rather high thermal stability and mechanical strength [24].

Similar reaction with pyrimidine containing diamines can be performed involving itaconic and citraconic anhydrides [25].

In order to increase the flexibility of polyimide chains and obtaining of the polymers with a greater elasticity the authors [26] have synthesized diamine **122** with two diphenyloxide fragments where the oxygen atoms play a role of a peculiar kind of hinges.



Scheme 14.

One should also consider another structural type of pyrimidine containing diamines wherein the oxygen bridge immediately separates the aminophenyl groups and the pyrimidine ring. The synthesis of such a monomer 2,5-bis(*p*-aminophenoxy)-4,6-diphenylpyrimidine **123** has been carried out in several stages with the total yield amounting to 40 %, starting from *o*-nitrophenoxyacetophenone and benzalbisurea [27] (Scheme 14).

The interest with respect to diamino derivative **123** is caused by an aspiration for obtaining heat-resistant polymers on its base those exhibit fusibility, solubility in organic solvents and good elasticity parameters [28].

#### REACTIVITY OF AMINOPHENYL PYRIMIDINES WITH THE PARTICIPATION OF AMINO GROUPS

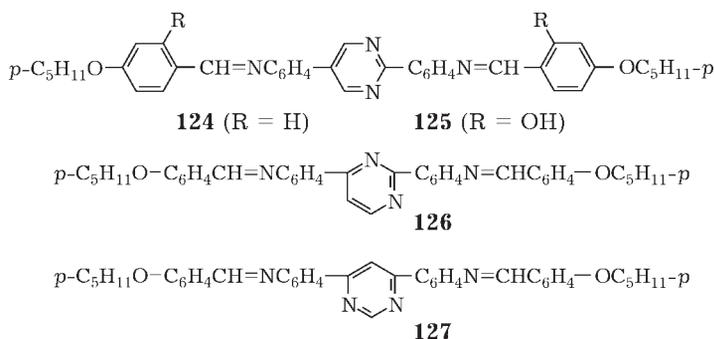
The reactivity of aminophenyl pyrimidines synthesized could be judged by the values of basicity constants  $pK_a$ , determined using the method of potentiometric titration [15]. For bis- and tris(aminophenyl)pyrimidines the value of  $pK_a = 6.0-4.0$ , which provides a normal formation of high-molecular PAA those could yield the polyimides of high quality [1]. Besides  $pK_a$  constants being the averaged values those reflect the acid-base equilibrium with participation of not only aminophenyl groups, but also heterocyclic nitrogen atoms, in order to estimate the reactivity of aminophenyl pyrimidines the authors of [29] used chemical shift values for the protons of amino groups in  $^1H$  NMR spectra, adequately describing their reactivity. It has been demonstrated that the protons of *meta*-amino groups in bis(aminophenyl)pyrimidines exhibit the resonance in a more strong

field ( $\delta = 5.22-5.30$  ppm) as compared to *para*-amino groups ( $\delta = 5.51-5.74$  ppm), which indicates a lower basicity of *para*-amino substituted species [11]. Comparing the chemical shifts  $\delta NH_2$  for 2,4-, 2,5- and 4,6-diamines for compounds **85**, **110** and **86** the following order of their reactivity has been determined:  $2,5 > 2,4 \sim 4,6$ -diamines, respectively [30].

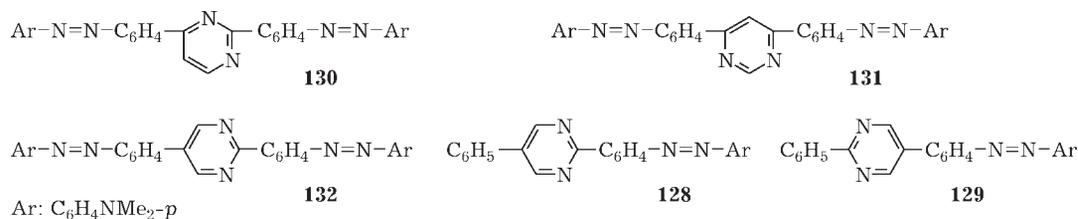
The same sequence of the reactivity was observed in the studies on the reaction kinetics for acylation of these diamines by maleic anhydride [30].

Basing on the data concerning the reactions of aminophenylpyrimidines with the amino group participation the processes of acylation, condensation with aromatic aldehydes, diazotization and the subsequent obtaining of azo compounds and azides have been investigated, since the compounds formed in these reactions could be of practical interest [15]. The acylation of bis(aminophenyl)pyrimidines by dianhydrides of aromatic tetracarboxylic acids results in the obtaining of heat-resistant and high-strength polyimides. The differences in reactivity of isomeric diamines **85**, **86** and **110** in the reactions of acylation were indicated earlier. It has been also demonstrated that the reaction of acylation could be used as a method for the purification of diamines since the acylamino derivatives are formed with high yields, and the subsequent acid hydrolysis of the latter results in obtaining high-purity diamines [15].

Schiff bases (anils) were obtained for diamines **85**, **86** and **110** under condensation with *p*-amyloxy benzaldehyde and *p*-amyloxy salicylic aldehyde. Anils **124** and **125** exhibit a high-temperature smectic polymorphism with a wide range of anisotropic melt. Isomeric anils **126** and **127** have not displayed liquid crystal properties [31] (Scheme 15).



Scheme 15.



Scheme 16.

Basing on aminophenyl pyrimidines **111** and **112** monoazo dyes **128** and **129** have been obtained, whereas diamines **85**, **86** and **110** have yielded bisazo dyes **130–132** [32] (Scheme 16).

For dyes **130–132** the UV spectra exhibit a bathochromic shift of the long-wave absorption band in comparison with dyes **128** and **129**, therewith the orientation of azo groups in isomeric structures **130–132** does not influence the position of this band. The obtained monoazo dyes **128** and **129** demonstrate liquid crystal properties forming a nematic anisotropic melt, whereas bisazo dyes **130–132** have not displayed mesomorphic properties [32].

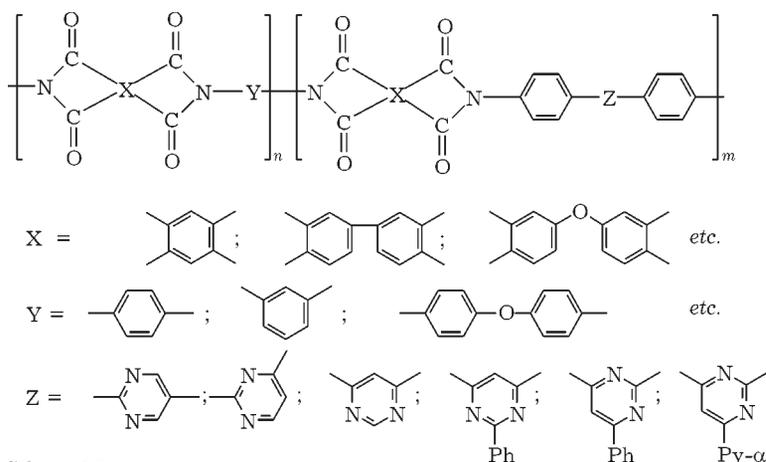
It has been shown that the luminescent properties exhibited by mono- and bis(*p*-aminophenyl)pyrimidines could be used in analytical quality control for dianhydrides of aromatic tetracarboxylic acids applied for the manufacture of polymers [33, 34].

#### POLYIMIDES BASED ON AMINOPHENYL PYRIMIDINES

The synthesized aromatic diamines containing the pyrimidine ring were entered into the reaction of polycondensation with dianhydrides

of aromatic tetracarboxylic acids such as pyromellitic acid, diphenyltetracarboxylic acid, diphenyloxyltetracarboxylic acid and others commonly used in the polymeric chemistry in order to obtain corresponding PAA as well as for the further multi-stage thermal imidization (Scheme 17). The investigation of the polymers obtained from the imidization has revealed a group of polyimides those are promising for the creation of polymeric materials. Basing on them films and fibres have been obtained those exhibit high-level thermal properties and deformation strength characteristics [14, 22, 23, 26, 35–39].

Basing on 2,5-diamine **110**, polyimide films and fibres have been obtained those are comparable with or even surpassing the best domestic and foreign similar samples in the deformation strength parameters and thermal stability [1, 22, 23, 37–41]. High thermal and strength characteristics are also exhibited by polyimides obtained basing on diamines **28**, **29**, **85**, **86** [14, 26, 36]. Approximately the same parameters concerning the thermal stability, but lower ones with respect to the strength properties are exhibited by polyimides based on 2-phenyl-4,6-bis(*p*-aminophenoxy)pyrimidine



Scheme 17.

**122** [26, 36]. The insertion of the pyrimidine fragment into the dianhydride component results in the formation of polyimides ranking below in the strength properties, but surpassing in thermal stability the polyimides where the same fragment is inserted into the diamine component [26, 36].

By comparing the properties of polyimides synthesized from 2,4- and 4,6-diamines (**85** and **86**, respectively) it was established that polyimides based on 4,6-diamine exhibit slightly better strength characteristics [26]. At the same time polyimides obtained from 2,5-diamine **110** are characterized by the highest parameters as compared to other pyrimidine containing polyimides, which could be caused by a linear structure of this 2,5-isomer [14, 26, 35]. Moreover, the polyimides based on the latter exhibit the highest thermal stability. As it is believed, the presence of the fragments of 2,5-diamine **110** in the macromolecules of polyimide provides a maximum number of contacts along the whole length of adjacent polymeric chains and, consequently, a complex of high strength and thermal stability properties [42]. It is, to all appearance, this fact that could explain the circumstance that the researches concerning the synthesis and studying the properties of pyrimidine containing polymers are mainly devoted

just to polyimides and co-polyimides with the use of 2,5-diamine **110** (Table 1).

Outstanding strength and thermal properties of pyrimidine polyimides are explained by the feature of the supramolecular structure, namely by a high density of packing of polymeric chains, realized through a level-by-level stacking of these chains. With such stacking a strong intermolecular interaction between the imide fragments of adjacent polymeric chains is provided. In the case of polyimides obtained from 2,5-diamine **110** the interchain interaction can occur also due to specific contacts between the imide fragments of one chain and the nitrogen atoms of the pyrimidine cycles of the other chain. Owing to this fact the pyrimidine cycles serve as an additional amplifier of the interchain interaction in polyimides, thus causing the strength and thermal stability to increase. Such a kind of stacking that is named a shearing one is considered to take place in co-polyimides with the participation of 2,5-diamine **110**, too [7, 43–45]. The insertion of the rigid fragments of 2,5-diamine **110** into co-polyimides results in a certain straightening of the macromolecule, a decrease in number of bends and a lower extent of molecular convolution, which improves both the thermal stability and strength properties. Thus, co-polyimides exhibit

TABLE 1

Deformation strength and thermal properties of polyimide films

Polyimide composition	Physicomechanical properties			Mass loss temperature, °C			Ref.
	$\sigma$ , MPa	$\epsilon$ , %	$E$ , GPa	$\tau_0$	$\tau_5$	$\tau_{10}$	
PM-DADPhE	160	40	3.5	390	470	517	[1]
PM-BZD	200	2	0.7	410	500	530	[1]
PM-DADPhE/PRM	312	43	6.5	450	540	560	[15]
PM-PRM	243	8	8.4	480	520	550	[35]
DPh-PRM	452	37.7	8.9	465	560	580	[23]
DPh-PPh/BZD	537	46	11.2	500	620	640	[22]
DPh-BZD/PRM	579	49	11.5	550	620	630	[22]
DPh-PPh/PRM	613	65	12.4	560	635	645	[22]
Kapton	172	70	3.0	–	–	–	[41]
Novax	343	50	6.9	–	–	–	[41]
Upilex S	392	30	8.8	–	–	–	[41]
LARC-CPI	448	15	10.3	–	–	–	[41]

Notes. 1. PM – pyromellitic dianhydride, DPh – dianhydride of diphenyltetracarboxylic acid, PRM – diamine **110**, BZD – benzidine, DADPhE – diaminodiphenyl ether, PPh – *p*-phenylenediamine. 2. The dash means the absence of data.

TABLE 2

Deformation strength and thermal properties of co-polyimide fibres IVSAN with the use of 2,5-diamine **110**

Polyimide composition	Physicomechanical properties			Mass loss temperature $\tau_5$ , °C	Ref.
	$\sigma$ , cN/tex	$\epsilon$ , %	$E$ , GPa		
IVSAN-87	103	9.5	35	470	[38]
IVSAN-89	170	3.3	248	570	[39]
IVSAN-90	360	4.8	282	560	[37]
Arimide T	60	8	15	420	[1]
Arimide VM	75	3.2	34	420	[38]
PRD-14	62	13	10	–	[1]

either an optimum combination or a considerable improvement of operational characteristics. It is illustrated by a number of examples of obtaining co-polyimides (films and fibres) with the use of 2,5-diamine **110** [22, 37–40, 46–49] (see Tables 1 and 2).

It should be noted that the work concerning the synthesis and studying the properties of homo- and co-polyimides based on this diamine carried out by the Chinese authors of [40], repeats the investigations performed by Russian colleagues within in 1980–1990ths [7, 18, 20, 22, 23, 35, 49].

Important results have been obtained in the comparative studies on the thermal oxidation stability of polyimides based on bis(amino-phenyl)pyrimidines others heterocyclic diamines and pyromellitic dianhydride. An increased thermal stability the some pyrimidine polyimides was noted: a 50–70 % mass loss is observed at the temperature values higher than 600 °C, whereas for the other polyimides such process occurs at lower temperature values [36].

Studies on the processes of carbonisation and graphitising of polymers are of a great interest, which is connected with the problem of the development of high-temperature sorption-filtering fibrous materials, selective gas separation membranes and carbonaceous reinforcing fibres [50]. From this standpoint the works are of importance concerning the studies on the role of the pyrimidine cycle in polyimides made of 2,5-diamine **110** as a structurizing factor in the carbonization process resulting in the formation of especially heat-resistant carbonizates [7].

As one would expect, the polyimides obtained basing on 2,5-bis(*p*-aminophenoxy)-4,6-diphenylpyrimidine **123**, exhibit the fusibility

and solubility in organic solvents those are necessary for the processing into production. At the same time the data those allow one to judge the thermal stability and deformation strength properties of these polymers are not presented in [28].

The polymers with three-dimensional structure formed due to the polymerisation of the products of amines addition to C=C multiple bond of bismaleimides, bisitaconeimides, bis-citraconimides, rank below aromatic polyimides in thermal stability, but these compounds could be processed into production without evolution of any volatile products and with no formation of porosity defects within the ware. The obtained polymers of such type containing the pyrimidine cycle in bisimide or diamine fragments are characterized with the mass loss beginning at 350–440 °C [25]. Some of pyrimidine containing oligo-bisitaconiimides as hardener reactoplastics have been recently used for the creation of composite proton conducting polymeric membranes [51].

## CONCLUSION

High-level functional characteristics of new polymeric materials developed on the base of polyimides with pyrimidine cycles in the polymeric chain allow one to use the products made of such materials under a wide range of extreme thermal conditions as well as to apply them to a number of modern engineering fields, such as microelectronics, aeronautical and space engineering, shipbuilding.

Realizing some of above mentioned schemes for obtaining pyrimidine containing diamines those are used as monomers offers considerable scope for scaling and technological development of corresponding chemical processes at

certain stages. It is demonstrated that co-polyimides based on pyrimidine diamines and aromatic analogues advantageously differ in operational characteristics from homopolyimides.

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