

УДК 541.64: 536.4

**E. T. Krut'ko, M. V. Zhuravleva, A. A. Martinkevich, N. R. Prokopchuk**  
Belarusian State Technological University

### POLYIMIDE USE IN PHOTOLITHOGRAPHY PROCESS

Polyimides thanks to the unique properties such as thermal stability, good mechanical and electrical characteristic, resistance to high energy a wide temperature range, excellent planarization popular in engineering and technology, particular in microelectronics. The production efficiency can be improved by providing photoresist properties to the polyimide materials using in microelectronics technology due to reduction of process steps and low bad production. Conversation is about, the creation of photosensitive polyimides negative and positive type containing reactive groups, which can be capable of being polymerized by UV-light with photo initiator. The main aim of this work increase the sensitivity, resolution and heat resistance of the material, on the base of a photosensitive polyimide composition. A new photosensitive polyimide composition based on polyamide acid solution in an organic solvent, tetramaleinamidoacid with the light-sensitive component. As show in the article, the possibility to create polymer cross-linked structure which can explain solubility difference after UV-radiation exposure in the chemical natural of the compounds. The composition has shown good results in photosensitivity and other properties.

**Key words:** microelectronics industry, polyamide acid, tetramaleinamidoacid, photosensitive polyimide composition, the polymer structuring.

**Introduction.** One of the most important conditions for the successful development of modern technology is a further improvement of semiconductor microelectronics as well as increasing its efficiency and product quality. It largely depends on the electrical and other properties of the materials, including polymers. These parameters determine the semiconductor affecting their stability under extreme conditions in a wide temperature range under the action of high-energy radiation and other factors.

In recent years, polyimide materials have become indispensable in many areas of new technology because of the unique properties of these polymers: high thermal stability, good mechanical and electrical performance, resistance to high energy stored within a wide temperature range, excellent plane. Methods of polyimide materials layers applying are simpler than of inorganic dielectrics.

Photoresists are new materials in the semiconductor industry. They are light-sensitive compounds used in the manufacture of integrated circuits. With their help, in some areas of semiconductor wafers create a protective film. It is a mask for the subsequent etching of the oxide layer of silicon topography. Photoresists are also used for the production of photomasks.

Technology for creating integrated circuits by using polyimide as interlayer dielectric includes operations involving the use of a photoresist for patterning the insulating layer under the action of light wavelength 340–430 nm. The operating principle of photoresists and photolithography is that as a result of interaction of light with the photosensitive component of the photoresist changes the physico-chemical properties, especially solubility and volatility exposed layer areas not protected by

the mask (template). It allows the subsequent manifestation to remove unexposed (negative process) or exposed (positive process) places, and thus to get relief image in the resist layer. The thus obtained relief (contact mask) is then a protective layer by selective etching or metallizing the substrate surface in the open areas allowing to transfer a relief image on a semiconductor substrate [1–8].

In the positive photoresists the film forming polymer that is dissolved in alkalis is combined with a hydrophobic photosensitive dissolution inhibitor. Under the influence of light as a result of photochemical reactions and subsequent thermal reactions the inhibitor is destroyed or converted to the hydrophilic product that can be dissolved in bases (e.g. carboxylic acid) and, therefore, the exposed areas of the inhibition of dissolution of the polymer are eliminated. The exposed and protected from light pattern areas demonstrate sharply differing solubility in alkalis, allowing you to create a relief when manifestation.

In the modern microelectronic technology are widely used positive photoresists, in which as a polymer base are used a low molecular weight phenol or cresol formaldehyde resin with a molecular weight of 500–900, and as the dissolution inhibitor are used *o*-naphthaquinonediazid, for example esters of 2,3,4-trihydroxybenzophenone, 2,4-dihydroxybenzophenone, di-(2-hydroxynaphthyl)methane and 5-sulfonic acid 2-diazo-1-naphthalinone (Fig. 1).

Widespread use of this type of photoresists is associated with an optimum combination of high sensitivity to exposure light with good resolution and stability with fluid and plasma etching technology layers. A significant advantage of positive photoresists compared with the negative is the use of relatively low toxic aqueous-alkaline developers [9].

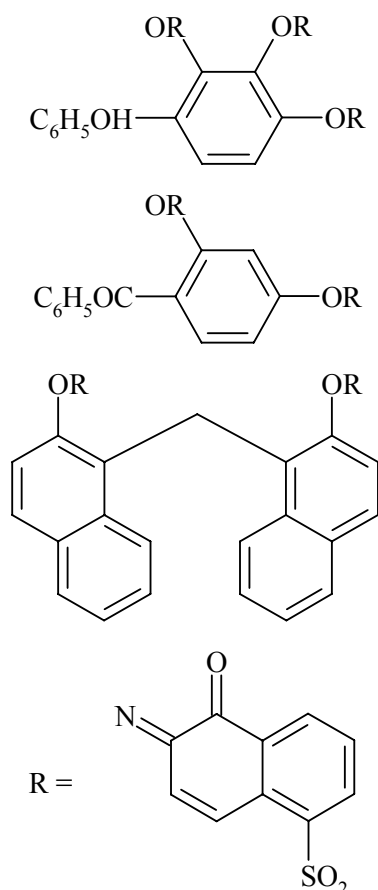


Fig. 1. o-naphthaquinondiazides

However in practice, often a number of photolithographic operations (e.g., opening of contact holes) is more profitable to implement using the negative photoresist, although the latter ones are generally inferior in positive photoresist on resolution. The absence of equivalent negative photoresist has given rise to so-called inverse photolithography, whereby a negative (inverted) image is on the positive photoresists.

An important advantage of the inversion image technology is the ability to control the shape of the profile of the manifest relief, ensuring accurate reproduction of specified sizes in the manifest relief and rectangular profile. By inversion technology, if necessary (for example, when implementing an explosive lithography) the negative manifestations of the wedge can be fairly easy obtained. A significant advantage of inverse photolithography technology is the possibility of reducing the range of photoresists, especially purchased by import.

Lithographic process comprises the following steps:

- the application of the photoresist;
- drying of the photoresist;
- exposure of the photoresist layer;
- display of the photoresist layer with simultaneous or subsequent etching of the polyimide layer;
- the removal of the photoresist layer.

Giving polyimide materials used in microelectronics technology the photoresist features allows improving the efficiency of production of integrated circuits by reducing the number of process steps and increasing the percentage of product yield. It enables to create some photosensitive polyimides of negative and positive type containing reactive groups that are capable to be easily polymerized under UV light in the presence of photoinitiator [10–11]. In the case of negative polyimide compositions containing usually grafted double bonds, irradiation with UV light leads to the formation of a crosslinked network structure and loss of solubility of irradiated portions. In contrast, the positive type polyimides after exposure become soluble in a developer system. The creation and application of negative and positive type photosensitive polyimide composition allows to simplify, modernize and intensify the microlithographic process.

This ability to create photosensitive polyimide compositions makes them particularly promising for applications in new fields of technology. A lot of information about possibilities to create photosensitive polyimide compositions and about their usage in modern microelectronics has been appeared in the scientific and patent literature in recent years [12–15].

Several photosensitive polyimide compositions used in microelectronics are well known quite long enough. For example, a composition containing a polyamic acid units, polyesteramides and polyimide is prepared in the mixture with N-methylpyrrolidone, diglyme condensation of dianhydride with diamine supplemented with bis-azide. However, this photosensitive polyimide composition does not have enough good photoconductive properties.

Also photosensitive polyimide composition consisting of a polyamic acid derivative, biszodibeniliden-methylcyclohexane, N-fenildietanolamine, Michler's ketone, 2-methoxyethanol, N-phenylethanolamine, N-phenyl-N-methylethanolamine, N-phenyl-N-ethylethanolamine is well known. However, its disadvantage is the complexity of the production process, non-reproducibility of the properties and insufficiency of high heat resistance.

Furthermore, it is known that there is a photosensitive polyimide composition that contains a polyamic acid obtained by reacting aromatic tetracarboxylic acid dianhydrides with diamines, and as a photosensitive compound – polieframidoasid obtained by esterification of the polyamic acid and an organic solvent. The disadvantage of this composition is its low thermal stability (up to 430°C). The quantities resolution and sensitivity are insufficient at introduction of polyefiramidoacid photosensitive compound due to the reduction of the performance of the polymer.

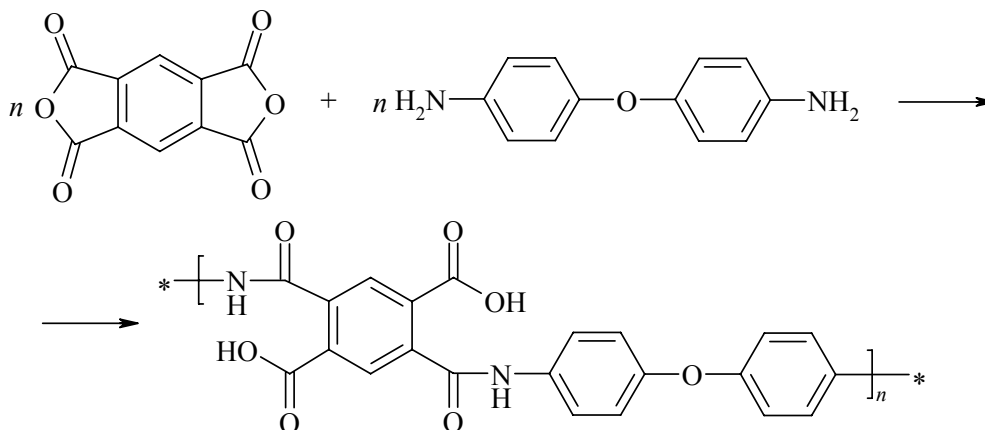


Fig. 2. Polyamide acid production

**Main part.** The aim of this work was to increase the sensitivity, resolution and heat resistance of the material, produced with using a photosensitive polyimide composition. For this reason it was proposed photosensitive polyimide composition based on polyamic acid solution (Fig. 2) in an organic solvent containing tetramaleinamide acid, and as the photosensitive component 2,6-di(4'-azidobenzal)-4-methylcyclohexanone was used.

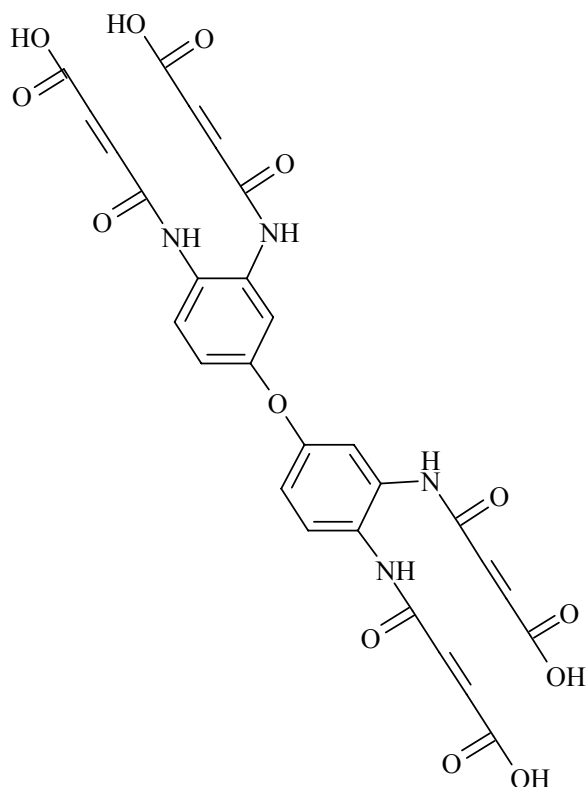


Fig. 3. Formula of tetramaleinamide acid

The basis of the proposed light-sensitive composition is a polyamide acid, the resulting low-temperature polycondensation of pyromellitic acid dianhydride and 4,4'-diaminodiphenyl ether in dimethylformamide (DMF).

Then, the resulting solution was introduced with continuous stirring the determined amounts of tetramaleinamide acid (TMAA) and 2,6-di(4'-azidobenzal)-4-methylcyclohexanone (DCH) which formulas are shown in Fig. 3 and 4 respectively.

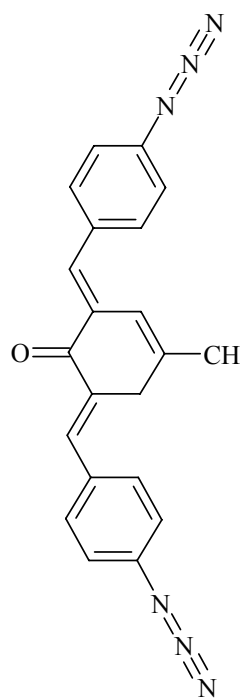


Fig. 4. Composition of 2,6-di(4'-azidobenzal)-4-methylcyclohexanone

The studies found that the individual or pair wise use of any of the components of the inventive composition doesn't provide the possibility for forming a pattern in the exposure conditions. Any effect to give to photosensitive polyimide composition some properties required in the pattern forming film and its subsequent resolution superior in heat resistance, sensitivity and resolution of the previously known polyimide composition is only achieved by using all three components combined proposed.

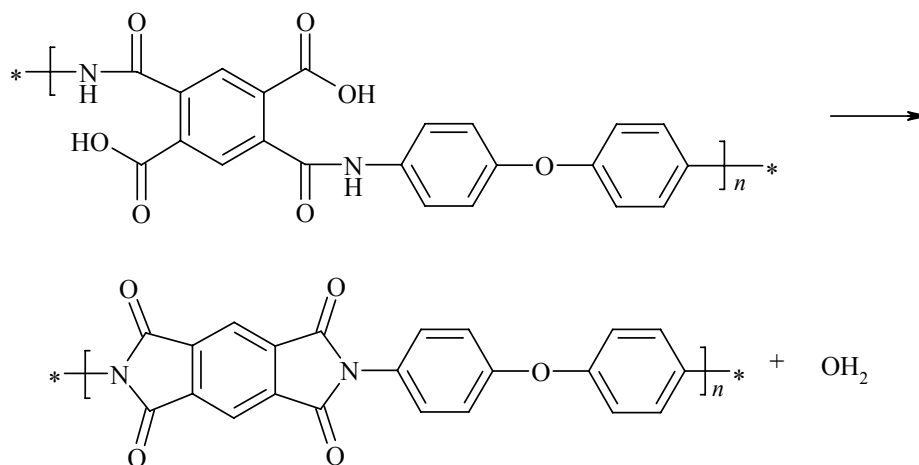


Fig. 5. Polyamide acid imidization

While the experimentally determined ratio of the components in the composition may vary within quite narrow limits.

The content in the polyamide acid composition by weight less than 12.251% does not provide a film-forming ability, and more than 12.594 wt % results in a reduction of sensitivity and resolution. TMAA content of the composition by weight less than 2.513% does not provide sufficient sensitivity and resolution, and 4.909 wt % leads to a loss of the composition film-forming ability. The content of the composition with at least 0.605 wt % of DCH does not provide sufficient resolution and sensitivity (exposure time increases more than 10 minutes). A growth of DCH content 0.857 wt % does not affect the change of the sensitivity and the resolving power (exposure time polyimide material is 9 minutes, remaining constant, but there is an excess crystallization photosensitive components on the surface of polyimide film).

Photosensitive compositions with the ratio of the components within the specified limits were prepared.

The composition was stirred and centrifuging at a rotational speed of the centrifuge of 3,000 revolutions/min. then it is applied to the substrate. It is dried at 95–100°C for 10 minutes, it is irradiated for 9 minutes, for 15 minutes it is exhibit by the following mixture: acetone : atsetilethyleneglycol monomethyl ether: dimethylformamide (1 : 1 : 1) wt %). Afterwards it is washed with deionized water, dried in a centrifuge and then heated for 20 minutes at 380°C, this is accompanied by imidization of PAA.

Edge image remains clear and it is not changed by heating to 450–470°C. Circuit element on the photomask (2.5 microns) is reliably reproduced by using this photosensitive composition. The results are shown in the Table.

Apparently, the use of these three components allows for the drying conditions of exposure and subsequent hardening of layer to form a polymer system in locations exposed to UV-exposed (window photomask), three-dimensional grid, which density is determined by quantitative content at the specified qualitative composition providing at further manifestation of different solubilities of exposed and unexposed areas.

#### Properties of developed compositions

No.	Content of photosensitive compositions, wt %				Exposure time, min	Minimum size of reproduced element, microns	Temperature limit save of the image configuration, °C
	PAA	TMAA	DCH	DMFA			
1	12.251	4.909	0.857	81.983	9.0	2.5	450
2	12.421	3.726	0.726	83.127	9.0	2.5	450
3	12.594	2.519	0.605	84.282	9.0	2.5	460
4	12.241	4.896	0.680	82.183	fragile film		450
5	12.602	2.521	0.679	84.198	12.0	3.5	450
6	12.565	2.513	0.830	84.092	9.0	2.5	470
7	12.282	4.913	0.726	82.079	fragile film		450
8	12.282	2.502	0.726	84.490	12.0	3.0	450
9	12.411	3.726	0.529	83.334	12.5	3.0	450
10	12.411	3.726	0.942	82.921	DCH crystallization		450

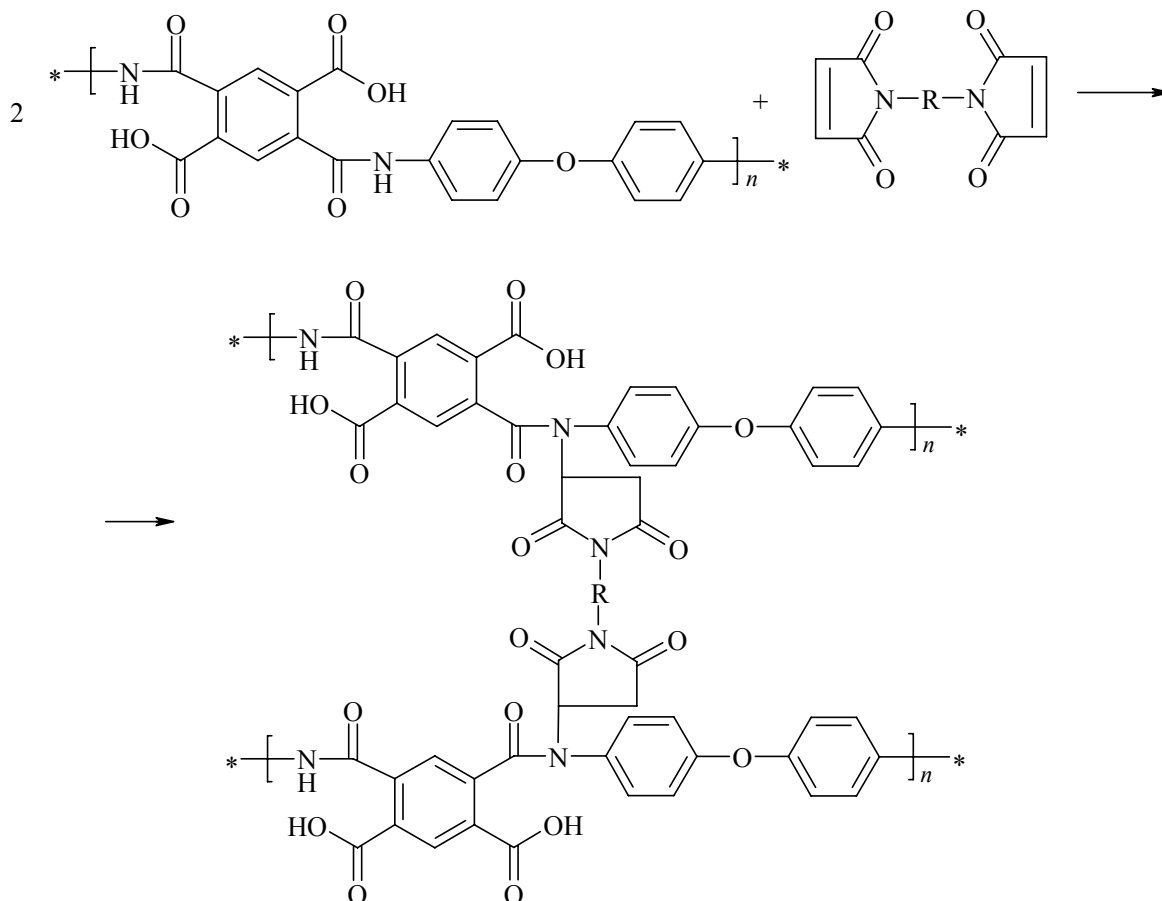


Fig. 6. Transformation diagram for a model system bis-maleimide PAA

A prerequisite possibility of creating a mesh structure of the polymer resulting in different solubility of its sections after exposure to UV light is the chemical nature of the used compounds. There are four multiple bonds in tetramaleinamidoacid molecule. They are strongly activated by the presence of adjacent carboxylic groups that causes them more interaction with high efficiency and  $\text{NH}_2\text{-NH-}$  polyamic acid groups when exposed to light, as in the case of bismaleinimidov. Scheme of transformations on the example of PAA-bis-maleimide model system is shown in Fig. 6.

Similar reaction of multiple bonds in the maleic fragments are possible with terminal amino groups of PAA molecules. Tetrafunctional cross-linking reactions of polyamic TMAA are obvi-

ously more complicated, though going by the same mechanism.

Possibly, this effect is the possible structuring polymer further enhanced by introducing DCH capable under UV light to generate free radicals, which enhance the effect on the polyamic acid crosslinking the exposed areas.

**Conclusion.** The researches show the best results in sensitivity, characterized by the exposure time and resolution, characterized by the exposure time and resolution, the size of the playback IC element and heat resistance were obtained for compositions 3 (Table). Thus, the proposed composition allows the composition to obtain a photosensitive polyimide-based material with a higher sensitivity, resolving power and heat resistance as compared with the prior art.

### References

1. Krut'ko E. T., Prokopchuk N. R., Martinkevich A. A., Drozdova D. A. *Poliimidy. Sintez, svoystva, primeneniye* [Polyimides. Synthesis, properties, application]. Minsk: BSTU Publ., 2002, 304 p.
2. Jinda T., Matsuda T. Sen I Gakkaishi, 1986, vol. 42, no. 10, p. 554.
3. Ahne H., Rubner R. Application of polyimides in electronics. Photosensitive polyimides. Lancaster, Technomic, 1995, pp. 13–48.
4. *Svetochuvstvitel'nye polimernye materialy* [The light-sensitive polymer materials]. Ed. by A. V. El't-sov. Leningrad, Khimiya Publ., 1985, p. 296.
5. Chuang K. C., Kinder J. D., Hull D. L., McConvill D. B., Youngs W. J. Polyimides based on noncoplanar 4,4'-Biphenyldiamines. *Macromolecules*, 1997, vol. 30, no. 23, pp. 7183–7190.

6. M. J. M. Abadie. *Bulletin de la Societe Française des Ingenieurs plasticiens*, 1987, no. 33, pp. 33–36.
7. Marc J. M. Abadie. La cinétique pour les produits photosensibles. *Europ. Coat. Journal*, 1993, no. 7, pp. 518–525.
8. Krut'ko E. T., Drozdova D. A., Prokopchuk N. R., Abadi M. Photosensitive polyimides. *Trudy BGTU* [Proceedings of BSTU], series IV, Chemistry, Technology of Organic Substances and Biotechnology, 2000, issue VIII, pp. 73–80.
9. M. J. M. Abadie. Photosensitive polyimides synthesis and applications. *Roum. Chem. Q. Rev.*, 1995, vol. 3, no. 3, pp. 229–246.
10. Dubois J. C., Bureau J. M. Photosensitive Polyimides. *Polyimides and other High-Temperature Polymers*, 1991, no. 1, pp. 461–470.
11. Loisel B., M. J. M. Abadie. Kinetic studies of photosensitive polyimides by photocalorimetry (DPC). *Polyimides and other High-Temperature Polymers*, 1991, no. 1, pp. 471–492.
12. Hideo Kaji. Photosensitive resin composition U.S. Patent Japan, no. 056682448, 1997.
13. Kenji Kojima. Aromatic polyimide used for positive-type photoresists U.S. Patent Japan, no. 2712621, 1998.
14. Asano Masaya, Hiramoto Hiroo. Photosensitive Polyimides. Lancaster, Technomic, 1995, pp. 121–152.
15. Feng Wei, Li Zuobang, Zhu Purun, Wang Lixin, Li Fang. Recent progress in photosensitive polyimides. *Gongneng Gaofenzi Xuebao*, 1996, vol. 9, no. 1, pp. 125–136.

#### Information about the authors

**Krut'ko Elvira Tikhonovna** – DSc (Chemistry), Professor, Professor, the Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: ela\_krutko@mail.ru

**Zhuravleva Maria Victorovna** – researcher, the Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: masha\_zhur@mail.ru

**Martinkevich Alexander Alexandrovich** – PhD (Chemistry), Assistant Professor, Assistant Professor, the Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: tnsippm@belstu.by

**Prokopchuk Nikolai Romanovich** – Corresponding Member of the National Academy of Sciences of Belarus, DSc (Chemistry), Professor, Professor, the Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: tnsippm@belstu.by

Received 23.12.2016