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### SOLUBLE BLOCK COPOLYIMIDES

**Keywords:** polyimides, copolyimides, oligo(amic acid), geometric parameters, conformation, block copolyimides, structural characteristics, identity period.

*Fragmentary polyamicacids on the basis of industrially made poly(4,4'-diaminodipheniloxide)pyromellitimic acid and oligoamidoacid, received by polycondensation of 4,4'-diaminodipheniloxide and dianhydride 4,8-diphenyl-1,5-diazodicyclo-/3,3,0/-octane-2,3,6,7-tetracarboxylic acid has been synthesized with their subsequent chemical imidization. Unlike initial poly(4,4'-dipheniloxide)pyromellitimide synthesized block polyimides possess solubility in polar aprotic solvents. For explanation of their solubility calculations of parameters of conformation of constitutional repeating units of macromolecules by computer modeling has been carried out.*

**Ключевые слова:** полиимиды, сополиимиды, олиго(амидо кислоты), геометрические параметры, конформация, блок сополиимиды, структурные характеристики, период идентичности.

*Фрагментарные полиамидокислоты на основе промышленно выпускаемых поли(4,4'-диаминодифенилоксид)пиромеллитамидокислоты и олигоамидокислоты, полученных путем поликонденсации 4,4'-диаминодифенилоксида и диангида 4,8-дифенил-1,5-дiazодидицикло-/3,3,0/-октан-2,3,6,7-тетракарбоновой кислоты были синтезированы с их последующей имидизацией. В отличие от исходного поли(4,4'-дифенилоксид)пиромеллитимида синтезированные блок полиимиды растворяются в полярных апротонных растворителях. Для объяснения их растворимости были проведены расчеты параметров конформации конституционных повторяющихся звеньев макромолекул с помощью компьютерного моделирования.*

### Introduction

One of the current trends in the polyimides' synthesis is the creation of fusible and soluble in organic solvents materials [1–7]. This allows to extend the range of their practical use and refines the classical methods for thermoplastics. This problem is particularly relevant in cases when the traditional scheme of high temperature prepolymer conversion into the final polymer, which usually takes place in the final product, can not be carried out due to thermal instability of the product elements. It is often achieved by the use of monomers (diamines and dianhydrides) with bulky side groups for the synthesis of polyimides [8–12].

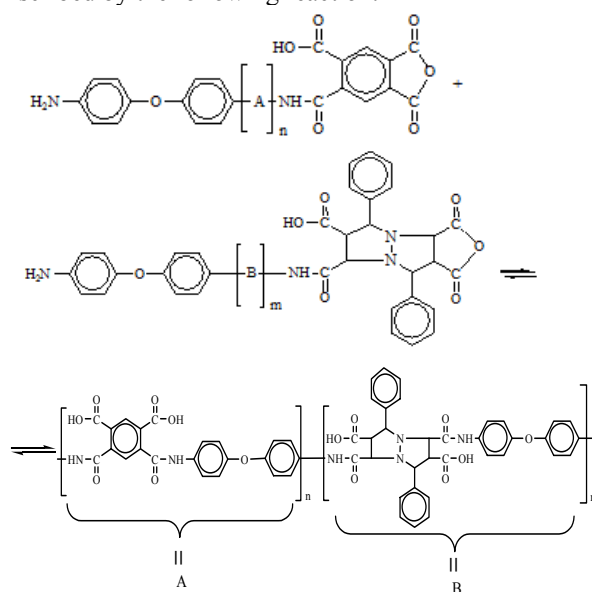
The synthesis of polymers from a mixture of several diamines and dianhydrides, and especially the synthesis of block copolyimides, represents wide opportunities of directed regulation of polyimides properties, including giving them solubility. One of the methods of the block copolymers synthesis is getting them on the basis of pre-synthesized oligomers with determination molecular weight and with different functional groups.

In this research, the synthesis of poly(4,4'-dipheniloxide)pyromellitimic acid (PAA), fragmented by oligo(amic acid) (OAA), obtained by low-temperature polycondensation of 4,4'-diaminodiphenyl oxide and dianhydride 4,4'-diphenyl-1,5-diazobicyclo/3,3,0/octane-2,3,6,7-tetracarboxylic acid and its subsequent chemical imidization. In the opposition to the original poly-(4,4'-aminodiphenyl)-pyromellitimide (PI) synthesized block copolyimides (BSPI) have a solubility in polar aprotic solvents. The parameter of BSPI conformation was calculated to explain its solubility.

### Subject and methods of research

The synthesis of fragmented poly(amic acids) was implemented by adding into 13% solution of PAA

in dimethylformamide (DMFA) OAA as a dry substance in quantities of 3, 4, 5, 7, 9, 12, 15, 20, 25 wt. % of the content of dry PAA in solution. The relative viscosity of the 0.5% solution of PAA in DMFA was 1.87, similar characteristic of OAA was 1.23. The interaction is described by the following reaction:

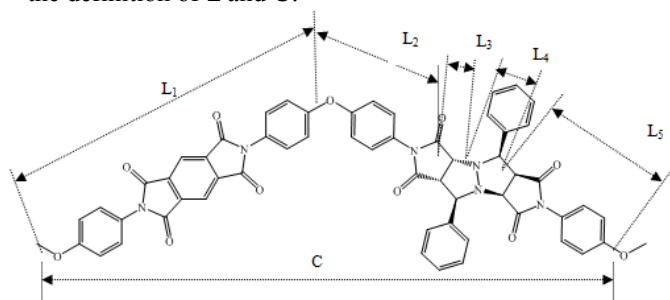


The transformation of the synthesized block copolymers which consists of fragments of PAA (A) and OAA fragments (B) into polyimide was realized by two ways – chemical and thermal [13].

The research of the spectral characteristics of the synthesized block copolyimide films was performed on FTIR spectrometer Nicolet 7101 in the frequency range 4000–300 cm<sup>-1</sup>.

For defining the geometric parameters of the polyimide macromolecules fragments semi-empirical quantum-chemical calculations were carried out using Hamiltonian PM6 model [14] with software package

MOPAC 2009. All geometric parameters of the three systems, including two elementary level of poly(4,4'-diphenyloxide) piromellitimide (PI), oligoimide based on 4,4'-diaminodiphenyloxide and dianhydride 4,8-diphenyl-1,5-diazobicyclo[3,3,0]octane-2,3,6,7-tetracarboxylic acid (OI) and copolyimide (CPI), which contains links of PI and OI were fully optimized in order to determine the structural characteristics. According to the calculated geometric parameters the values of the identity period  $C$ , and contour length of the fragment of the macromolecular chains in the range of a period of identity  $L$  were determined. Figure 1 shows the plane projection of the synthesized block copolymer fragments based on PAA and the OAA and illustrates the definition of  $L$  and  $C$ .



**Fig. 1** □ The scheme of block copolyimide fragments to determine its structural characteristics

Conformation parameter  $K_{\pi}$  was calculated to quantify the crookedness and curl of different nature soluble block copolyimides fragments [15-19]:

$$K_{\pi} = \frac{L - C}{C} \cdot 100\%; \quad L = \sum_{i=1}^n L_i$$

where  $C$  – identity period along the polymer chain, Å;  $L$  – contour length of the chain skeleton within a period of identity, Å.

## Results and discussion

It was experimentally established that synthesized OAA well combine with a solution of aromatic PAA and can be introduced into it by dissolving by stirring for 2-2.5 hours with up to 20 wt. % from the content of aromatic PAA (in terms of dry matter) to the form of a homogeneous clear solution in DMFA. However, film-forming ability of these compositions only retains if the content of the input oligomer PAA is less than 9 wt. %. Exceeding of these limit results leads to bursting and loosing the ability to form a uniform film by the fragmented polymer after removal of the solvent by drying in air at room or elevated temperature to 50-60°C. Lower limit of the content of the OAA, ensuring the achievement of the target properties of the composition, is 4 wt. %. Its fewer content in substance does not provide solubility to chemically imidized compositions.

It was studied the kinetics of transformation macromolecules of synthesized BSPI prepolymers by IR spectroscopy [13] in order to optimize the process of obtaining fragmented polyimides. The comparison of the intensity of the absorption bands of imide rings with a peak at 1380  $\text{cm}^{-1}$  before and after the chemical imidi-

zation showed that the maximum degree of imidization is 92-93% and it is reached within 60 min. In a similar way it was established that after thermal imidization by step increase of temperature up to 320°C within 120 min maximum degree of imidization of the block copolyimides is 86-87%.

It is found that the rate constant for the initial stage of the chemical imidization of blok copoly(amic acids) measured at temperatures of 22, 35 and 45°C, are about two times higher than the rate constants of this stage of the thermal imidization, measured at 170, 185 and 205°C. In this case, the activation energy of the chemical imidization is  $72 \pm 5$  kJ/mol, and for the process of thermal imidization is  $87 \pm 5$  kJ/mol, which is according to the literature data [13]. These peculiarities of the process, probably due to the fact that the mobility of the carboxyamide links in the liquid phase of the chemical imidization are much higher than in the condensed phase at a solid thermal imidization.

It should be emphasized that the synthesized chemically imidized blok copolyimide in contrast to a similar polymer obtained by thermal imidization, soluble in polar aprotic solvents – dimethylformamide, dimethylacetamide, dimethylsulfoxide, N-methylpyrrolidone, forming a normal solution concentration up to 5 wt. % from which coatings with high electrophysical characteristics can be obtained.

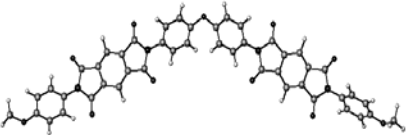
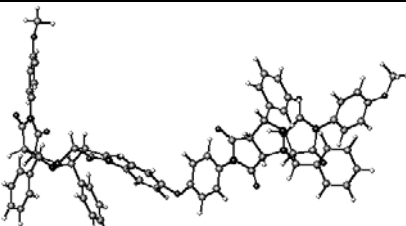
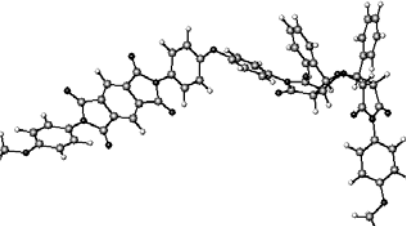
Apparently this is due to the fact that under mild conditions of the chemical imidization flowing in solution under the influence of dehydrating reagent mixture in the polymer intermolecular interactions difficult, leading to the loss of polymer solubility. Oligoamic acids fragments containing voluminous diphenyldiazobeziclooktan links create difficulties for the intermolecular interactions.

It is of a great interest to determine the causes of acquisition of block copolyimides solubility. In this respect the analysis of the structural and conformational properties of the polymer dives is useful information.

In real materials the individual molecules are not isolated from each other. There are always certain interchain interaction between them, whose energy depends on the chemical nature of the parts of the macromolecules and the density of packing. The distance between the interacting atoms and atomic groups in neighboring macromolecules depends on the conformation of the macromolecular chains. It is shown on the example of aromatic and cycloaliphatic polyimides [6, 8] that there is a clear correlation between the energy of intermolecular interactions and conformational parameter  $K_p$ . Conformational parameter  $K_p$  reduces in the transition from the saddle geometric structure of cycloaliphatic dianhydride to plane geometry of piromellitic dianhydride, and from the broken structure of "flexible" diamines to a flat linear structure of "hard" diamines, packing density of the macromolecules and intermolecular interaction energy are increases. That is one of the causes of solubility of aromatic polyimides.

Table 1 shows the three-dimensional fragments of elementary components of PI, OI, and CPI and shows the values of the identity periods ( $C$ , Å), contour length of the chains within a period of identity ( $L$ , Å), and the conformational parameters ( $K_p$ ).

**Table 1 - Conformations and structural characteristics of three-dimensional block copolyimides fragments**

Фрагмент макромолекулы	L, Å	C, Å	K <sub>P</sub> , %
 PI	6,014	32,752	9,9
 OI	9,472	24,150	63,0
 CPI	37,75	27,74 4	36,0

The data presented in the table show that the conformational parameter is minimal for elementary units of PI based on pyromellitic dianhydride and 4,4'-diaminodipheniloxide because bending of the polymer chain is only in the "hinge" oxygen atom diamine fragment of the repeating unit of the macromolecule. The elementary unit of OI has a much higher value of conformation, because of the collapse fragment chain macromolecules as bending occurs not only in the "hinge" oxygen, but in fragments diazobicyclooctan dianhydride acid. In elementary links of CPI with fragments of PI and OI, due to the combination of rigid fragment of PI and OI strongly curved fragment conformational parameter takes an intermediate value, which, however, is 3.6 times higher the value of the IP for the aromatic fragment (PI). High values of the conformational parameters and hence the low level of intermolecular interactions helps to create a more "loose" structure, the penetration of the solvent molecules between the polymer chains, their salvation, swelling and dissolution.

### Conclusion

Thus, the results of the research indicate that it is possible to use oligoamic acid based on 4,4'-diaminodipheniloxide and dianhydride 4,4'-diphenyl-1,5-diazobicyclo[3,3,0]octane-2,3,6,7-tetracarboxylic acid which have a volumetric three-dimensional structure and block the implementation of interactions between aromatic PAA macromolecules as copolymer.

We can get polyimide film-forming materials with high dielectric properties, which are soluble in aprotic amide solvents by chemical imidization.

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