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)pyromellit(amic 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-tetracarboxilic 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 aprotonic 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-1. 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-tetracarboxilic 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 KΠ was calculated to quantify the crookedness and curl of different nature soluble block copolyimides fragments [15-19]: ; 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 imidizied 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 cm-1 before and after the chemical imidization 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±5 kJ/mol, and for the process of thermal imidization is 87±5 kJ/mol, which is according to the literature data [13]. These pecularities 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 imidizied 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 KP.

Conformational parameter KP 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 (KP). Table 1 - Conformations and structural characteristics of three-dimensional block copolyimides fragments Фрагмент макромолекулы L, Å C, Å KP, % PI 36,014 32,752 9,9 OI 39,472 24,150 63,0 CPI 37,751 27,744 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'-diaminodipheniloxside 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-tetracarboxilic 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