Introduction Interest to the processes proceeding at increased temperatures (up to 600K) in polymer materials is stimulated by a possibility to obtain systems with double conjugated bonds, which exhibits the properties of semiconductors. Intensity of formation of the polyconjugation systems increases with temperature, if pyrolysis proceeds in vacuum or under inert atmosphere[1,2]. Intramolecular transformations with further change of supermolecular system were studied well on the example of polyacrylonitrile [3]. Thermal transformation of polyacrylonitrile leads to formation of a polymer, consisted of condensed pyridine cycles with conjugation by C=C bonds, as well as by C=N ones. Concentration of paramagnetic particles increases with temperature of pyrolysis. It is known that the ESR signal is one of the signs of polyconjugation appearance in polymer systems [4]. Deep physical and chemical transformations in polymers proceed at combination of temperature varying with introduction of various donor-acceptor inorganic or organic additives into the reactor. It is known that one of the ways of obtaining of organic semiconductors is the pyrolysis of of low or high molecular substances. However, as a rule, this method allows a formation of powder like materials and formation of monolithic ones is connected with additive technological procedures, after which often the material deteriorated. The main aim of the presented work is the obtaining of pyrolized monolithic materials with wide range of the electric conductivity. Experimental Epoxy resin (ER), novolac phenoloformaldehyde resin (PFR), polymethyl-silsesquioxane (PMS) and fiber glass (FG) were chosen as the initial substances. Pyrolysis of mixtures of the components mentioned, pressed in press-forms, was conducted at various temperature ranged within 500 - 1500 K in 10 Pa vacuum. Products obtained in this manner possess good mechanical and electroconducting properties, and are monolythic materials. Pyrolized samples or pyrolyzates were tested by polarization microscopy technique in order to determine their microstructure. The paramagnetic properties of pyrolizates were investigated by using of ESR spectrometer of Brukker type. The type and mobility of charge carriers investigated were measured by the Hall effect technique. The main aim of the presented work is the obtaining of pyrolized monolithic materials with wide range of the electric conductivity. Results and Discussion Inclusion of fiber glass into compositions was induced by the following idea. It is known [5] that at high temperatures organosiloxanes react with side hydroxyl groups, disposed on the fiber glass surface. In this reaction they form covalent bonds with those side groups. It is known that after high-temperature treatment silsesquioxanes obtain a structure, close to inorganic glass with spheres of regulation due to formation of three-dimension siloxane cubic structures and selective sorption of one of the composite elements is possible on the filler surface in the hardening composite [5]. Figs. 1 -6 reflect changes of some mechanical, electric and paramagnetic properties of polymer composites depending on pyrolysis temperature. These dependences are the result of proceeding of deep physicochemical transformations in materials. Combined analysis of the change of microstructure and density of materials (Fig. 1) with the increase of

pyrolysis temperature induces a conclusion that excretion of some volatile fractions of organic part of the material, carbonization of organic residue and caking of glassy fibers cause the increase of pyrolyzate density, based on the composite with polymethylsesquioxane. The limit of pyrolyzate density is reached at temperatures near1273 K (Fig.1, curve 1), followed by a decrease of the material density due to intensification of thermal degradation processes with pyrolysis temperature increase above 1273 K. Fig. 1 - Dependences of rden (1) and strengthening at elongation s (2) on pyrolysis temperature for the composite ED-20 + PFR + KO-812 + FG The material strengthening at elongation extremely depends on the pyrolysis temperature, possessing an intermediate maximum near 1273 K (Fig.1, curve 2). Burning out of organic part of the composite leads to weakening of adhesion forces in the interphase and, consequently, to decrease of the material strengthening with pyrolysis temperature increase up to a definite value. At further increase of pyrolysis temperature on the curve of this dependence the small maximum appears due formation of covalent chemical bonds between glass and organic conjugated double bounds skeleton. At more high temperatures of pyrolysis the degradation of these bonds has place The conductivity (g) and charge carrier mobility of the pyrolyzates grows monotonously initially with increasing of the pyrolysis temperature and then saturate. This dependence points out a constant accumulation of polyconjugation systems due to complex thermochemical reactions. Chemical bonds which link organic and inorganic parts of the composite reliably increase stability of polyconjugated structures, responsible for electrically conducting properties of materials. The electrically conducting system of the materials can be considered as a heterogeneous composite material, consisted of highly conducting spheres of polyconjugation and barrier interlayers between them. The most apparently true model of electric conductivity in materials with the system of double conjugated bonds seems to be the change transfer in the ranges of polyconjugation possessing metal conductivity and jump conductivity between polyconjugation spheres [6]. An important information on the nature of conductivity of pyrolized polymer materials is given by investigation of the g dependence on temperature. Comparison of the experimental data on dependence of g - T with known for organic semiconductors [2]: g = g0 exp (-dE/kT) (1) and one proposed by N. Mott shows that the dependence obtained by us experimentally satisfies to Mott low [7]: (2) where T0 and g0 are constants depending on some quantum mechanical values. Fig. 2 - Dependences of electric conductivity g (1), mobility of charge carriers m (2) on pyrolysis temperature for the composite ER + PFR + PMS + FG The growth of cariers mobility m well described with analogical expression: The dependence of paramagnetic centers concentration in pyrolized polymer composites on pyrolysis temperature has an extreme character (Fig. 7). Curve of the present dependence possesses maximum, which is corresponded to the 900 - 1000 K range. Change of the ESR absorption line intensity is accompanied by a definite change of its width. In this case, the form and width of the ESR line changes (at

constancy of the g-factor) - lines are broadened, and asymmetry of singlet occurs. Maximum on the concentration dependence for paramagnetic centers on pyrolysis temperature is correspondent to the temperature range, in which volatile products of pyrolysis are released and polyconjugation systems occur. Decrease of concentration of the centers above 973 K proceeds due to coupling of a definite amount of unpaired electrons. According to this coupling new chemical structures occur (for example, polyconjugation responsible for electric conductivity increase). Fig. 3 - Temperature dependence of paramagnetic centers N (1), ESR line width (2) and ESR line assimetry parameter A/B (3) on the pyrolysis temperature for the ED-20 + PFS + KO-812 + FG composites At more high temperatures of pyrolysis deepening of thermo-chemical reactions in composites leads to formation of the paramagnetic centers localized on the oxygen atom. On the other hand, it is probable of the increase of free charges-current carriers contribution into ESR signal, the line of which is characterized by asymmetry (so called Dayson form [8]). Conclusions High-temperature treatment (pyrolysis) of polymer composites in the inert atmosphere or in the hydrogen medium stimulates processes of formation of the polyconjugation systems). Charge transfer between polyconjugation systems is ruled by the jump conductivity mechanism with variable jump length. In this case, its temperature dependence is described by the Mott formulas. Presence of a glassy fiber and polymethylsilsesquioxane in composites promote formation of covalent bonds between organic and inorganic parts of the composite at pyrolysis. This leads to improving of mechanical properties of materials together with the electric ones.