Introduction By Sergeev’s definition the nanochemistry is a science field connected with obtaining and studying of physical-chemical properties of particles having sizes of nanometer scale. Let’s note that according to this definition polymers synthesis is automatically a nanochemistry part as far as according to the Melikhov’s classification polymeric macromolecules (more precisely macromolecular coils) belong to nanoparticles and polymeric sols and gels – to nanosystems. Catalysis on nanoparticles is one of the most important sections of nanochemistry. The majority of catalytic systems are nanosystems. At heterogeneous catalysis the active substance is tried to deposit on carrier in nanoparticles form in order to increase their specific surface. At homogeneous catalysis active substance molecules have often in them selves nanometer sizes. The most favourable conditions for homogeneous catalysis are created when reagent molecules are adsorbed rapidly by nanoparticles and are desorbed slowly but have high surface mobility and, consequently, high reaction rate on the surface and at the reaction molecules of such structure are formed at which desorption rate is increased sharply. If these conditions are realized in nanosystem with larger probability than in macrosystem, then nanocatalyst has the raising activity that was observed for many systems. In the connection such questions arise as adsorption and desorption rate, surface mobility of molecules and characteristics frequency of reagents interaction acts depend on the size, molecular relief and composition of nanoparticles and the carrier. The presence paper purpose it the application of fractal analysis for description of polymerization kinetics in nanofiller presence. Results and Discussion The analysis of polymerization processes in nanofiller presence does not differ principally from the one for transesterification model reaction [1]. In the present chapter some important aspects of such polymerization will be studied, mainly on the example of solid-phase imidization. The authors [2] studied the kinetics of poly (amic acid) (PAA) solid-state imidization in nanofiller (Na+-montmorillonite) presence and found an essential reaction acceleration both at imidization temperature Ti raising in the range 423-523K and Na+-montmorillonite contens Wc increase within range 0-7 phr. In paper [2] the possible chemical mechanism of Na+-montmorillonite action as a catalyst was offered, assuming larger contact surface area and respectively larger number of reaction active sites, that promotes dehydration and imide ring closure reaction. This model has hypothetical and qualitative character. However, it became obvious lately, that on chemical reactions kinetics large influence can be exercised by purely physical factors such as reactionary medium connectivity [3] or macromolecular coil structure [4], which in all polymer’s states (solution, melt, solid phase) is fractal [5, 6]. It is also well known [7], that the fractal objects description is correct only within the framework of fractal geometry and the usage in such case of Euclidean geometry gives approximation more or less corresponding to reality. Proceed from the said above the authors [8, 9] exercised the solid-state imidization reaction description both in nanofiller presence and in its absence within the framework of structural (fractal) models. In the general and the simplest form solid-state imidization reaction can be represented by the equation [3]: , (1) where A is a reagent (in considered case PAA). Then for such reaction description the following relationship was used [3]: , (2) where rA is the concentration of nonreacted reagent A, which further will be accepted equal to (1-Q) (Q is a conversion degree), t is a reaction duration, ds is a spectral dimension. In Fig. 1 the dependences rA=(1-Q) on t in log-log coordinates, corresponding to the relationship (2), for imidization reaction without filler at the four indicates above imidization temperatures Ti = 423, 473, 503 and 523K are shown. As follows from the data of Fig. 1, all the four adduced plots are linear, that allows to determine the value of spectral dimension ds. The estimations have shown, that the imidization temperature Ti raising within the range 423-523K results to ds increase from 0.42 up to 1.68, i.e. to essential growth of reactionary system connectivity degree. In Fig. 2 the similar dependences for various Na+-montmorillonite contents Wc at fixed Ti = 473K are shown. As one can see, nanofiller introduction exercises much weaker influence on ds value than the imidization temperature raising [9]. Fig. 1 The dependences of rA=(1-Q) on t in log-log coordinates, corresponding to the relationship (2), for PAA solid-state imidization without filler at temperatures: 423 (1), 473 (2), 503 (3) and 523 (4) [8] ds increase at Ti raising for the same reactionary system, shown in Fig. 1, assumes, that in the considered case ds should be considered as an effective spectral dimension ds', depending on reactionary medium heterogeneity degree [10]. The medium heterogeneity degree can be characterized by heterogeneity exponent h, which changes within the range 01 and turns into zero only for homogeneous samples [10]. The values h and are connected with one another by the equation [10]: . (3) Fig. 2 The dependences of rA=(1-Q) on t in log-log coordinates, corresponding to the relationship (2), for PAA solid-state imidization at temperature 473 K and Na+-montmorillonite contents Wc: 0 (1), 2 (2), 5 (3) and 7 (4) phr [8] In Fig. 3 the dependence h(Ti) is shown, from which fast decrease h or reactionary medium homogeneity raising follows at Ti increase. At Ti » 540K the exponent h = 0, i.e. the reactionary medium becomes homogeneous. The authors [2] have shown, that for the studied polyimides the melting temperature Tm is equal about to 800K. Proceeding from the known law of two-thirds [11]: , (4) the glass transition temperature Tg of polyimide can be estimated as equal to ~ 533K. In other words, as it was expected [12, 13], reactionary medium in solid-state imidization case became homogeneous (Euclidean) at glass transition. The shape of the curve h(Ti), shown in Fig. 3, i.e. tendency for h®0 at temperature raising, assumes, that the fractal-like effects, namely, ds' variation, are connected with energetic disorder [10]. Fig. 3 The dependence of reactionary medium heterogeneity exponent h on imidization temperature Ti for PAA solid-state imidization at Na+-montmorillonite contents Wc: 0 (1), 2 (2) and 5 (3) phr [8] Let's consider physical principles of reactionary system connectivity degree change, characterized by effective spectral dimension ds', at imidization temperature Ti and Na+-montmorillonite contents Wc change. As well as earlier, the value of macromolecular coil fractal dimension Df can be estimated with the help of formula [4]: , (5) where c1 – is constant, determined according to the boundary conditions and accepted equal to 8´10-4 s-1 for studied reactions, k1 is reaction rate constant. In Fig. 4 the dependence of ds’ on Df is shown, from which it follows, that ds’ increases at Df reduction and at Df ®1.50 (transparent macromolecular coil [5]) the value ds’ has a fast tendency to its limiting magnitude ds’=2.0 [10]. Such form of dependence ds’(Df) allows to make two conclusions. Firstly, the definite interconnection of ds’ and Df characterized by the curve of Fig. 4 exists. Secondly, the value ds’ can not be considered as spectral dimension of proper macromolecular coil, since in this case theory assumes ds’ decrease at Df reduction [14]: , (6) where d is dimension of Euclidean space, in which fractal is considered (it is obvious, that in our case d = 3). Proceeding from the said above, let’s assume, that in the considered case ds’ is a reactionary medium connectivity indicator, in some way connected with macromolecular coil structure characterized by dimension Df. Let’s consider one of the possible theoretical schemes of such interrelation. It is well known [15], that in chemical reactions large effect has steric factor p (p£1) showing that not all collisions of reagents occur with proper for reaction products formation orientation of reacting molecules. The value p is defined by dimension Df and can be calculated according to the equation [4]: . (7) Fig. 4 The dependence of reactionary medium effective spectral dimension ds’ on macromolecular coil fractal dimension Df in imidization process. The notation is the same, as in Fig. 3 [8] As it follows from this equation, the value p is increased at Df reduction. Macromolecular coil sites number N, capable to take part in a chemical reaction (active sites), is determined like that [16]: . (8) Let’s pay attention, that N~ρA-1 in the relationship (2). But in case of a chemical reaction not all active sites of macromolecular coil can react in virtue of the condition p1, but only their part Np, proportional to p. For preliminary estimations it can be assumed [9]: . (9) Believing that for imidization reaction without filler at Ti = 423K Df =2.12, ds’=0.42, i.e. experimentally determined values, one can calculate the value p according to the equation (7), the value Np according to the equation (9) and to determine constant coefficient in the relationship (8) at t =const=15 min., which is equal to 2. Further, using this coefficient in the equation (8), one can calculate the values ds’, which further will be designated as (ds’)th, for imidization reaction with variable Ti and Wc. In Fig. 5 the comparison of values ds’, determined from the slope of plots rA(t) in log-log coordinates (see Figs. 1 and 2) and (ds’)th, calculated according to the equations (7)-(9), is shown. As one can see, between these parameters a good correspondence was obtained. This means, that reactionary space connectivity, characterized by dimension ds’, depends on macromolecular coil structure dimension Df and this dimension is specific namely for the chemical reactions owing to steric factor p introduction [9]. From the point of view of process chemistry this can be treated as follows: the smaller Df, is the more open macromolecular coil structure, is the easier dehydration process (water removal) and imidic ring closure proceed [2].

Fig. 5 The comparison of the calculated according to the relationship (2) ds’ and the equations (7)-(9) (ds’)th effective spectral dimension values of reactionary medium in imidization process. The notation is the same, as in Fig. 3 [8] Therefore, the data considered above demonstrated that the main parameter, controlling solid-state imidization rate, is the reactionary system connectivity degree characterized by its effective spectral dimension. In its turn, this dimension is a function of macromolecular coil structure that is polymeric reaction specific feature. Imidization temperature raising defines reactionary medium heterogeneity reduction and corresponding increase of its connectivity degree [8, 9]. In paper [17] the quantitative analysis of the imidization kinetics temperature dependence was given within the framework of one more conception, namely, a chemical reactions kinetics fractal model [4, 18]. The authors [17] have assumed that the cause of imidization reaction acceleration at its temperature Ti growth is polyimide macromolecular coil structure change, which is the consequence of its molecular characteristic as the last in paper [17] ratio C¥ was chosen, which is a polymer chain statistical flexibility indicator [19]. As earlier, the macromolecular coil structure is characterized by its fractal (Hausdorff) dimension Df. The interrelation between C¥ and Df is given by the equation [20]: . (10) The temperature dependence C¥ (and, consequently, Df) can be calculated, using the equation offered in paper [13]: , (11) where Tm is the melting temperature, for the studied nanocomposites equal to ~ 800K [2]. For the constant in the equation (11) determination the following method were used. The general equation of chemical reactions fractal kinetics is the formula [4]: , (12) where c0 is reagent initial concentration, h0 is initial viscosity of reactionary medium. By constructing the dependence Q(t) in log-log coordinates at Ti =523K the value Df =1.59 was determined, then from the equation (10) corresponding to it the value C¥ and according to the equation (11) – the value of estimating constant. Further for the remaining imidization temperatures the values C¥ were calculated (the general variation 3.51-4.51) and corresponding to them the values Df (the general variation 1.59-1.81). Then according to the equation (12) the kinetic curves Q(t) were calculated. The value of reactionary medium initial viscosity h0 in this case was accepted constant and equal to 1 (with taking into account of the fact that the reaction occurs in solid phase) and the value c0 was determined by the selection method at the condition of the best correspondence of theoretical and experimental curves Q(t). Simulation of kinetic curves of solid-state imidization carried out by the considered method is shown by points in Fig. 6. As one can see that a good correspondence of theory and experiment is obtained. The selection of reagents initial concentration (or reaction active centers) shows it increase within the range 6.5-35 of relative units at imidization temperature Ti growth within the range 423-523K. This c0 increase can also be explained within the framework of chemical reactions kinetics fractal conception according to which [4]: , (13) where M is molecular weight of reaction product, tgen is reaction duration. Fig. 6 The kinetic curves Q(t) of solid-state imidization at temperatures: 423 (1, 5), 473 (2, 6), 503 (3, 7) and 523K (4, 8). 1-4 – experimental data; 5-8 – the calculation according to the equation (12) [17] Assuming M = const, we obtain theoretical value c0(c0th) according to the relationship (13) [17]: . (14) Accepting as tgen imidization reaction part duration, on which the first order reaction laws are fulfilled and on which imidization mainly was ended, the authors [17] have estimated the values c0th, which are compared with the values c0, obtained by a selection method, in Fig. 7. As it follows from the data of this Figure, between the values c0th and c0 the linear correlation is observed, passing through coordinates origin. Such correspondence assumes, that the value c0 (imidization active centers number) increases at Ti raising at the expense of diffusive processes intensification [4]. Fig. 7 The relation of by selection obtained c0 and calculated according to the relationship (14) c0th number of imidization reaction active sites [17] Hence, the stated above results have shown, that the fractal conception of chemical reactions kinetic describes quantitatively kinetics of solid-phase imidization process at different temperatures. This description is given only within the framework of reaction physical aspects and does not affect its chemical aspects. The effective initial concentration of reagents c0 at imidization temperature growth is due to physical cause also – by reagents diffusion intensification in solid-phase state. It’s necessary to indicate that the nanofiller introduction in reactionary mixture results to two-phase system formation, where an important (or decisive) role will be played by interfacial interactions [21]. Particularly, the interaction of PAA-Na+-montmorillonite should result to the structure change of polyimide (PI) forming macromolecular coil [22] and similar effect gives the imidization temperature Ti raising [23]. Therefore the authors [24] fulfilled structural analysis of processes, occurring in solid-phase imidization reaction course, according to the aspect indicated above.