УДК 54.057

G. V. Kozlov, G. E. Zaikov, E. Klodzinska,
Richert Jozef

THE FRACTAL KINETICS OF POLYMERIZATION CATALYZED BY NANOFILLERS (PART 3)

Keywords: polymerization, kinetics, catalyst, nanofiller, fractal analysis, strange diffusion.

The fractal analysis of polymerization kinetics in nanofiller presence was performed. The influence of catalyst structural features on chemical reaction course was shown. The notions of strange (anomalous) diffusion conception was applied for polymerization reactions description.

Ключевые слова: полимеризация, кинетика, катализатор, нанонаполнитель, фрактальный анализ, аномальная диффузия.

Был выполнен фрактальный анализ кинетики полимеризации в присутствии нанонаполнителя. Было показано влияние структурных особенностей катализатора на ход химической реакции. Понятие странной (аномальной) диффузии было использовано для описания реакций полимеризации.

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

In previous parts of the article the solid-state imidization reactions were represented [1] and the interfacial interactions problems were considered [2].

As it is known [3, 4], a macromolecular coil in various polymer's states (solution, melt, solid phase) presents itself the fractal object characterized by fractal (Hausdorff) dimension D_f. Specific feature of fractal objects is the distribution of their mass in space: the density ρ of such object changes at its radius R variation as follows [5]:

$$\rho = \rho_{dens}\left(\frac{R}{a}\right)^{D_f - d}, \tag{1}$$

where ρ_{dens} is the density of material, which consists of fractal object in dense packing assumption, a is a lower linear scale of object fractal behaviour, d is the dimension of Euclidean space, in which fractal is considered (it is obvious, that in our case d=3).

From the equation (1) ρ decrease at D_f reduction follows, since it's always $D_f<d$, that, naturally, simplifies reagents access in macromolecular coil internal regions and results to the fuller chemical transformations, i.e. to conversion degree $Q_{\lim}$ increase. Besides, it is known [5] that at macromolecular coil formation by irreversible aggregation mechanisms in its central part densely-packed region is formed where the proceeding of reaction is impossible. Proceeding from that, it is possible to confirm, that for a chemical reaction only a part of macromolecular coil is accessible, which is the larger, the smaller its fractal dimension D_f is. In the transparent coil case ($D_f \le 1.5$ [3]) both low- and high-molecular substances can pass freely through it and this assumes, that in such case the value $Q_{\lim}$=1.0. At D_f=2.5 chemical reaction ceases and gelation process begins [6, 7]. This means, that at reaching D_f=2.5 $Q_{\lim}$=0. The indicated estimations allow to write the fractional exponent ν_f for chemical reactions similarly to the definition, accepted in paper [8]:

$$\nu_f = D_f - \left(D_f^{gel} - 1\right) = D_f - 1.5, \tag{2}$$

where D_f^{gel} is the value D_f at gelation, equal to 2.5.

Let's remind, that according to [9], the value ν_f characterizes the system states fraction unchanging in its evolution process. In case of chemical reactions generally and imidization process particularly this assumes, that the value ν_f characterizes the macromolecular coil part inaccessible for chemical transformations. Then the coil part β_{ac} accessible for such transformations is determined as follows [10]:

$$\beta_{ac} = 1 - \nu_f = 2.5 - D_f. \tag{3}$$

Proceeding from the said above, it's possible to define the limiting conversion degree $Q_{\lim}$ by the following identity [10]:

$$Q_{\lim} = \beta_{ac} \cdot \qquad (4)$$

Therefore, the estimation $Q_{\lim}$ brings to the question of fractal dimension D_f determination. As it was noted above, at present two methods of indicated dimension determination exist. The first method consists of using chemical reactions fractal kinetics general relationship, i.e. the equation (12) [1]. Besides, the calculation of dimension D_f allows to have the equation (5) [1].

Plotting the dependences $Q(t)$ in log-log coordinates allows to determine the value D_f according to the slope of these dependences in their linearity case according to the equation (12) [1]. In Fig. 1 the mentioned dependences for process of PAA imidization without nanofiller are shown. As one can see, these dependences are linear, that allows to make estimation D_f by the indicated method.

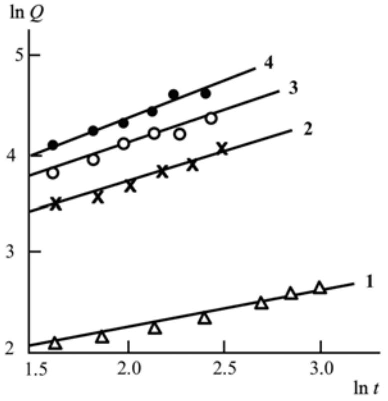

Fig. 1 - The dependences of imidization degree Q on reaction duration t in log-log coordinates for PAA imidization process at temperatures: 423 (1), 473 (2), 503 (3) and 523K (4) [11]

In Fig. 2 the comparison of the dimensions D_f calculated by two methods (D_{f1} and D_{f2}, respectively) is shown. As one can see, both methods give close values D_f and therefore further their average magnitude will be used, i.e. $D_f=(D_{f1}+D_{f2})/2$.

Further the parameter β_j can be estimated according to the equation (3) and compared with the limiting conversion degree $Q_{\lim}$, obtained experimentally [12]. Such comparison for PAA imidization process without nanofiller and in the presence of 2 mass.% of Na^+-montmorillonite at four temperatures of imidization indicated above is shown in Fig. 3 good enough correspondence of theory and experiment (their average discrepancy is equal to ~ 12 %) was obtained, that confirms the offered treatment correctness [11].

Hence, the data stated above assume, that limiting conversion (in the given case – imidization) degree is defined by purely structural parameter – macromolecular coil fraction, subjected to the evolution (transformation) in chemical reaction course. This fraction can be correctly estimated within the framework of fractal analysis. For this purpose two methods of macromolecular coil fractal dimension calculation have been offered, which give coordinated results.

It is known, that the majority of catalytic systems are nanosystems [13]. At the heterogeneous catalysis active substance is being tried to deposite on the carries in nanoparticles form in order to increase their specific surface. At homogeneous catalysis active substance molecules have often by them selves nanometer sizes. It is known too [12] that the operating properties of heterogeneous catalyst systems depend on their geometry and structure of surface, which can influence strongly on catalytic properties, particularly, on catalysis selectivity. It was shown [14] that the montmorillonite surface is a fractal object. Proceeding from this, the authors [15] studied the montmorillonite fractal surface effect on its catalytic properties in isomerization reaction.

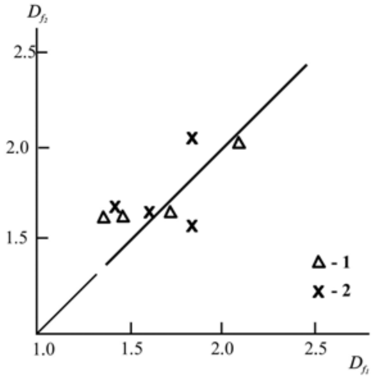

Fig. 2 - The comparison of macromolecular coil fractal dimension D_{f1} and D_{f2} calculated according to the relationships (12) and (5) [1], respectively, for PAA imidization process without filler (1) and in the presence of 2 mass.% of Na^+-montmorillonite (2) [11]

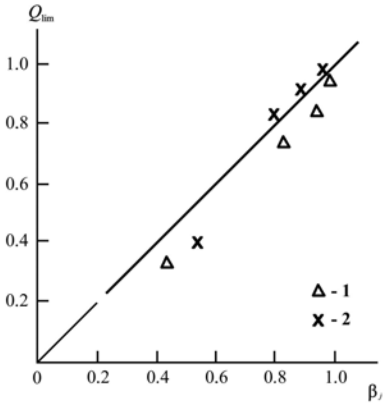

Fig. 3 - The dependence of limiting imidization degree $Q_{\lim}$ on parameter β_j value for PAA imidization process without nanofiller (1) and in the presence of 2 mass.% of Na^+-montmorillonite (2) [11]

In paper [15] two types of montmorillonite were used – Na- montmorillonite (SW) and Ca- montmorillonite (ST). The indicated types of layered silicate were applied as a catalyst at isomerization of 1-butene (B) by obtaining of cis-2-butene (C) and trans-2-butene (T).

Meakin [9] considered the simplest catalysis scheme, which was used later for estimation of catalyst selectivity S_c. It demonstrates general features, inherent to all catalysis models, and is expressed by a simple reaction scheme, which by analogy with the reactions (2.16)-(2.21) can be written as follows [16]:

$$\mathrm{A}+\mathrm{P}\rightarrow \mathrm{A}_a, \tag{5}$$

$$\mathrm{A}\underset{(cat)}{\overset{k_1}{\longrightarrow}}\mathrm{B}, \tag{6}$$

$$\mathrm{A}+\mathrm{A}_a\underset{(cat)}{\overset{k_2}{\longrightarrow}}\mathrm{C}, \tag{7}$$

where the reaction (5) presents itself molecule A adsorption on catalyst surface P. The reaction (6) presents itself unimolecular process, transformating adsorbed molecule A(A_a) in new molecule B, which is assumed as fastly leaving the catalyst surface. In real systems this can be an isomerization reaction (as in the considered case) or a reaction of secondary products decay. The reaction (7) presents itself molecule A addition to catalyst surface in the site already, occupied by the adsorbed molecule A(A_a) with subsequent reaction of molecule C formation, which is also assumed by fastly leaving this surface in order to make the model maximally simple. The selectivity S_c is determined as molecules C number, divided on molecules B number [17].

Within the framework of this model with using computer simulation the following expression for S_c was obtained [17]:

$$S_c=\frac{k_f\Sigma_i P_i^2/\left(k_1+2P_i k_f\right)}{k_1\Sigma_i P_i/\left(k_1+2P_i k_f\right)}, \tag{8}$$

where k_f is molecules A receiving rate on catalyst surface, P_i is contact probability for i-th site of the indicated surface.

The equation (8) is simplified essentially for two limiting cases. In the large k_1 limit it accepts the form [17]:

$$S_c=\frac{k_f}{k_1}\Sigma_i P_i^2, \tag{9}$$

and in the small k_1 limit let's obtain the equation

$$S=\frac{k_f}{Nk_1},$$

in which general number of surface sites N can be estimated according to the following general fractal relationship [18]:

$$N\sim L^{d_{surf}}, \tag{10}$$

where L is characteristic size of nanofiller particle, accepted equal to 100 nm [12], d_{surf} is catalyst surface fractal dimension.

In its turn, d_{surf} value can be estimated with the help of the relationship [19]:

$$S_u=410\left(\frac{L}{2}\right)^{d_{surf}-d}, \tag{11}$$

where S_u is a specific surface of nanofiller particles, d is dimension of Euclidean space, in which fractal is considered (it is obvious, that in our case d=3). The value S_u is given in m^2/g and L – in nm.

In Fig. 4 the dependence $S_c(N)$ is adduced for the two types of the studied catalyst – montmorillonite. In case of 1-butene isomerization reaction the equations (5)-(7) can be written as follows [16]:

$$\mathrm{B}+\mathrm{P}\rightarrow \mathrm{B}_a, \tag{12}$$

$$B_a\underset{(cat)}{\overset{k_1}{\longrightarrow}}C, \tag{13}$$

$$B+B_a\underset{(cat)}{\overset{k_2}{\longrightarrow}}T, \tag{14}$$

and then the value S_c is defined as the ratio T/C.

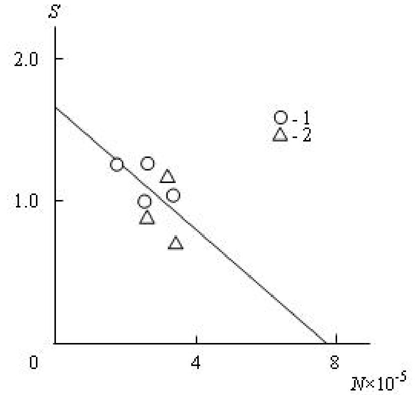

Fig. 4 - The dependence of the catalyst selectivity S_c on its surface sites general number N for Na- montmorillonite (1) and Ca- montmorillonite (2) [16]

From Fig. 4 data S_c linear decrease at N growth follows. According to the equation (5) this assumes isomerization reaction course at small k_1 and at fulfillment of the conditions k_1=const, k_f=const or k_f/k_1=const. In case of larger k_1 (the equation (9)) $\Sigma_i P_i^2>1/N$ [17]. For Witten-Sander clusters the value $\Sigma_i P_i^2$ is scaled as follows [17]:

$$\Sigma_i P_i^2\sim N^{-\gamma}, \tag{15}$$

where the exponent γ varies within the limits 0.5-0.8 [17].

One of the fractal analysis merits is a clear definition of limiting values of its main characteristics – fractal dimensions. So, the value d_{surf} changes within the limits $2\leq d_{surf}<3$ [20]. At d_{surf}=2.0 the value $N=0.1\times10^5$ relative units and according to the Fig. 4 plot maximal value S_c=1.65. At maximal for real solids dimension d_{surf}=2.95 [21] $N=7.94\times10^5$ of relative units and according to Fig. 4 plot $S_c\rightarrow0$. This means that at such conditions trans-2-butene conversion degree goes to zero.

It was found out d_{surf} increase results to the decrease of trans-2-butene and cis-2-butene general conversion degree. This is explained by the fact that the formed in synthesis process polymeric chain has finite rigidity and consists of statistical segments of finite length. In virtue of this circumstance it can not "repeat" the growing catalyst surface roughness at d_{surf} increase and "perceive" it as still smoother surface. In this case the effective fractal dimension of montmorillonite surface d_{surf}^{ef} is determined as follows [22]:

$$d_{surf}^{ef}=d_{surf}, \tag{16}$$

within the interval d_{surf}=2.0-2.5 and according to the equation (16) [2] (at d_{surf}^{ef} =d_{surf} and d_{surf}= d_{surf}^{0}) – within the interval 2.5-3.0.

For the studied catalysts the values d_{surf}=2.637-2.776. In Fig. 5 the dependence $Q(d_{surf}^{ef})$ is adduced, which turns out to be linear and is extrapolated to Q=0 at d_{surf}^{ef} =2.0 (or d_{surf}=3.0) and to Q=0 at d_{surf}^{ef}

$=d_{surf}$=2.5. Thus, the combined consideration of Figs. 4 and 5 allows to assume the catalyst optimal value d_{surf}, which is equal to 2.5. At this d_{surf} magnitude Q =1.0 and S_c=1.54, i.e. close to maximal value S_c for montmorillonite in the considered reaction.

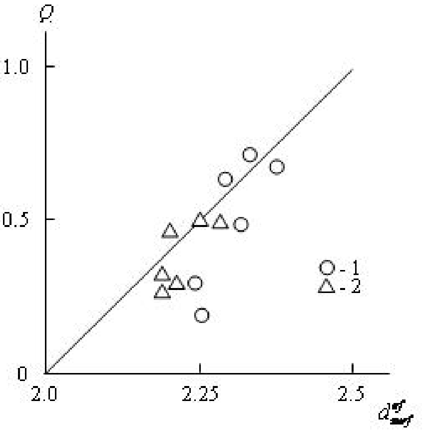

Fig. 5 - The dependence of general conversion degree Q on effective fractal dimension d_{surf}^{ef} of catalyst surface for Na- montmorillonite (1) and Ca- montmorillonite (2) [16]

Hence, the results stated above demonstrated the important role of catalyst (montmorillonite) surface fractal geometry in its catalytic properties definition [16].

Polymerization in situ (together with a filler) is often applied as a method for receiving nanocomposites. In paper [23] matrix epoxy polymer cross-linking process both in nanofiller (Na^+- montmorillonite) presence and without it was studied within the framework of a strange (anomalous) diffusion conception [24]. A nanocomposites epoxy polymer/Na^+- montmorillonite (EP/MMT) cross-linking was made at temperatures 353, 373 and 393K, cross-linking of EP – at 393K [25].

Let's remind the main postulates of a strange (anomalous) diffusion conception. As it is known [24], in general case diffusion processes are described according to the equation:

$$\langle r^2(t)\rangle \sim t^{\alpha}, \qquad (17)$$

where $\langle r^2(t)\rangle$ is mean-square displacement of a particle during time t.

If the exponent α=1 then the relationship (17) describes classical diffusion and if α≠1 – strange (anomalous) diffusion. Depending on concrete value α persistent (superdiffusive, $1<\alpha\le 2$) and antipersistent (subdiffusive, $0\le\alpha<1$) processes are distingnished. In the strange diffusion equation the parameter α has significance of "active" time fractal dimension, in which real particles walks look as random process; active time interval is proportional to t^{α} [24]. In its turn, the exponent β in this equation [24]:

$$\frac{\alpha}{\beta}=\frac{d_s}{d} \qquad (18)$$

accounts for simultaneous particles jumps ("Levy flights") from one turbulence region into another. The ratio of exponents α/β can be determined according to the equation (18), in which spectral dimension d_s is determined, in its turn, according to the relationship (2) [1].

The estimations have shown [23], that the introduction MMT in reactionary mixture increases substantially the value d_s: if for reaction without MMT d_s=0.027, then at MMT introduction d_s increases up to 0.175-0.452 and rises at cross-linking temperature increase. A macromolecular coil (microgel) fractal dimension EP D_f can be determined with the help of the relationship (12) [1] the account made according to the indicated ratio has shown, that the smallest value D_f equal to 1.52, is obtained for cross-linking reaction without MMT and at MMT introduction it increases up to 1.67-2.19.

The authors [23] have proceeded from the assumption, that the dependence Q on active time t^{α} should be linear and general for all the four studied reactions. The exponent β value was chosen on the base of this assumption. It turns out, that β decreases both at MMT introduction and at the temperature raising from 28 up to 3.8. Besides, at cross-linking reaction without MMT course the decrease β from 28 up to 9 is observed. In Fig. 6 the dependence $Q(t^{\alpha})$ for all the studied reactions is adduced. As one can see, the general linear correlation is obtained. The active time increases at MMT introduction: for reaction without MMT it makes ~ 2 % from the real one and at MMT presence it can reach 30%.

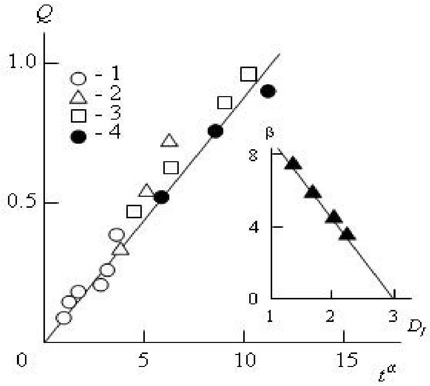

Fig. 6 - The dependence of cross-linking degree Q on active time t^{α} for reaction without MMT (1) and in MMT presence at T=353 (2), 373 (3) and 393K (4). In the insert: the dependence β(D_f) [23]

In the insert the dependence β on D_f is shown, from which β decrease at microgel fractal dimension growth follows. This assumes "Levy flights" probability decrease at the system viscosity increase. Hence, the ability to control active time gives the possibility of reaction course operation.

Conclusions

Thus, the present work results have been shown the applicability and usefullness of fractal analysis and strange (anomalous) diffusion conception for description of polymerization reactions, catalyzed by nanofillers. The nanofiller introduction in reactionary mixture results in two-phase system formation, where a decisive role will be played by interfacial interactions.

The polymerization conversion degree is defined by its active (fractal) time. Hence, the ability to control active time gives the possibility of reaction course operation.

References

1. Kozlov G.V., Zaikov G.E., Klodzinska E., Richert Jozef. The fractal kinetics of polymerization catalyzed by nanofillers. Vestnik Kazanskogo tekhnologicheskogo universiteta. – 2013. – T.16. – №15. – P.13-18.
2. Kozlov G.V., Zaikov G.E., Klodzinska E., Richert Jozef. The fractal kinetics of polymerization catalyzed by nanofillers (Part 2). Vestnik Kazanskogo tekhnologicheskogo universiteta. – 2013. – T.16. – №19. – P.188-193.
3. Baranov V.G., Frenkel S.Ya., Brestkin Yu.V. Doklady AN SSSR, 1986, vol. 290(2), pp. 369-372. (Rus.).
4. Vilgis T.A. Physica A, 1988, vol. 153(2), pp. 341-354.
5. Brady R.M., Ball R.C. Nature, 1984, vol. 309(5965), pp. 225-229.
6. Botet R., Jullien R., Kolb M. Phys. Rev. A, 1984, vol. 30(4), pp. 2150-2152.
7. Kobayashi M., Yoshioka T., Imai M., Itoh Y. Macromolecules, 1995, vol. 28(22), pp. 7376-7385.
8. Kozlov G.V., Batyrova H.M., Zaikov G.E. J Appl. Polymer Sci., 2003, vol. 89(7), pp. 1764-1767.
9. Nugmatullin R.R. Teoretich. i Matematich. Fizika, 1992, vol. 90(3), pp. 354-367. (Rus.).
10. Kozlov G.V., Shustov G.B. In coll.: International Interdisciplinary Seminar “Fractals and Applied Synergetics, FaAS-01”, Moscow, Publishers MSOU, 2001, pp. 155-157. (Rus.).
11. Naphadzokovz L.Kh., Kozlov G.V., Zaikov G.E. Electron. Zhurnal “Studied in Russia”, 111, p. 1173-1179, 2007, http: // Zhurnal. apl. relarn. ru / articles / 2007 / 111. pdf. (Rus.).
12. Tyan H.-L., Liu Y.-C., Wei K.-H. Polymer, 1999, vol. 40(11), pp. 4877-4886.
13. Melikhov I.V. Rossiiskii Khimichesk. Zhurnal, 2002, vol. 66(5), pp. 7-14. (Rus.).
14. Pernyeszi T., Dekany I. Colloid Polymer Sci., 2003, vol. 281(1), pp. 73-78.
15. Moronta A., Ferrer V., Quero J., Arteaga G., Choren E. Appl. Catalysis A, 2002, vol. 230(1), pp. 127-135.
16. Naphadzokovz L.Kh., Shustov G.B., Kozlov G.V. In cool.: Proceedings of 9-th International Symposium “Order, Disorder and Properties of Oxides, ODPO-2006”. Rostov-na-Donu, RSU, 2006, pp. 49-51. (Rus.).
17. Meakin P. Chem. Phys. Lett., 1986, vol. 123(5), pp. 428-432.
18. Stanley E.H. In book: Fractals in Physics. Ed. Pietronero L., Tosatti E. Amsterdam, Oxford, New York, Tokyo, North-Holland, 1986, pp. 463-477.
19. Naphadzokovz L.Kh., Aphashagova Z.Kh., Kozlov G.V. In coll.: V Intern. Sci.-Pract. Conf. “Effective Building Constructions: Theory and Practice”. Penza, PSU, 2006, pp. 271-273. (Rus.).
20. Avnir D., Farin D., Pfeifer P. Nature, 1984, vol. 308(5959), pp. 261-263.
21. Balankin A.S. Synergetics of Deformable Body, Moscow, Ministry of Defence SSSR, 1991, 404 p. (Rus.).
22. Van Damme H., Levitz P., Bergaya F., Alcover J.F., Gatineau L., Fripiat J.J. J. Chem. Phys., 1986, vol. 85(1), pp. 616-625.
23. Naphadzokovz L.Kh., Kozlov G.V. In coll.: Intern. Sci.-Techn. Conf. “Composite Building Materials. Theory and Practice”. Penza, PSU, 2006, pp. 170-172. (Rus.).
24. Zelenyi L.M., Milovanov A.V. Uspekhi Fizichesk. Nauk, 2004, vol. 174(8), pp. 809-852. (Rus.).
25. Chen J.-S., Poliks M.D., Ober C.K., Zang Y., Wiesher U., Giannelis E. Polymer, 2002, vol. 43(18), pp. 4895-4904.

© **G. V. Kozlov** – ст. науч. сотр. каф. высокомолекулярных соединений, Кабардино-Балкарский государственный университет; **G. E. Zaikov** – д.х.н., проф. каф. технологии пластических масс КНИТУ, ov_stoyanov@mail.ru; **E. Klodzinska** – PhD, Institute for Engineering of Polymer Materials and Dyes, Torun, Poland; **Richert Jozef** - PhD, Director of Institute for Engineering of Polymer Materials and Dyes, Torun, Poland.