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Nano-Scaled Intrachain Ordering and Dynamics in Two-Dimensional Orientational Polymer Domains [1)]

*Maximov A.V., Shevchenko S.S., Maximova O.G., and Gotlib Yu. Ya.**

Institute of Mathematics, Physics and Informatics, Cherepovets State University,
Soviet Prospect 8, Cherepovets, 162000 Russia, e-mail: max@csu.metacom.ru.

*Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi
Prospect 31, St. Petersburg, 199004 Russia, yygotlib@imc.macro.ru

SUMMARY: Statistical and local relaxation properties of two-dimensional finite polymer systems (domains) are considered. The domains consist of a large number of semirigid chains with the finite contour length at free, half-free and fixed boundary conditions for chain ends. The intermolecular orientational order at short distances between chains in the thick domains is similar to the order in infinite two-dimensional systems. The correlations of orientation between sufficiently distant elements of different chains decay by the exponential law, but the effective constant of interchain interactions in the domain is proportional to the molecular weight of the chain. At the given intra-and interchain interactions an elongtation of the chains leads to a local ordering of chains in the domain (at free boundary conditions) or, on the contrary, to the decreasing of the parameter of short-range orientational order (at fixed and half-free boundary conditions). Independently of type of boundary conditions the parameter of large-range orientational order tends to zero with increasing of the chain contour length.

Dynamical equations and relaxation spectrums for times of local motions are obtained. From time correlation functions of local relaxation the times of nano-scaled mobility of chains were calculated in depending on the bending rigidity of chains, the parameter of interchain interactions, and the contour length of chains. At the given intra-and interchain interactions an elongtation of chains forming the domain leads to to the slowing-down of local mobility of chains in the domain. The comparison with experimental date obtai-ned by dielectric relaxation and polarized luminescence methods on investigation of nano-scaled mobility in the dilute melts of comb-shaped polymers has been carried out.

Introduction

Molecular mobility of polymer chains is a sensetivite indicator of orientational order in partly ordered polymer systems with sufficiently segmental motions, e.g. in liquid-crystalline

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polymers [1]. Experimental label and impulse methods of study of intramolecular mobility, very intensively developed at the present time, allow to investigate in detail the behaviour of time dependences of orientational correlation functions and determine times of local motions of chains both in solutions and in the bulk [2].

At last time the models of reptation type [3] were used, as a rule, to describe large-scale correlations along the given polymer chain and corresponding motions in condensed polymer systems. Statistical multichain models [4] were proposed for study of conformational and relaxation properties of cooperative bending and translation motions of chains in infinitely extended polymer systems with short- and long-range orientational order [5, 6]. Rotation diffusion and local motions of chains in orientationally ordered layered structures are investigated only by the molecular or the Brownian dynamics methods (see, e.g. ref. [7-9]).

In the present paper parameters of intra- and intermolecular orientational ordering and times of local motions of chains in plane finite polymer systems – domains, will be investigated. The special study of two-dimensional models may be of practical interest in connection with properties of thin films, membranes and other surface or interfacial mesophase polymeric structures [10,11]. Individual macromolecules in dilute solutions of comb-shaped polymers owing sufficiently strong interchain orientational interactions of extended side chains may be considered in the first approximation as two-dimensional finite polymer systems with some intramolecular ordering [12]. Relationships, concerning of intra- and intermolecular ordering and relaxation behaviour of local properties, obtained in the present paper for extended domains of finite width – "stripes", will be used for interpretation of experimental date on the investigation of nano-scaled mobility in dilute melts of comb-shaped polymers.

Model: Boundary conditions

We suppose that a sufficiently large number M of polymer chains with a finite contour length are packed in the plane «quasi-lattice» (Fig.1). The chains consist of N rigid elements with the length l, oriented in a plane like rotators in the classical Vaks-Larkin model [13]. By description of ordered state of comb-shaped polymers the parameter N characterizes the contour length of side chains, and the number M is directly proportional to the length of the main chain, correspondingly (Fig.1).

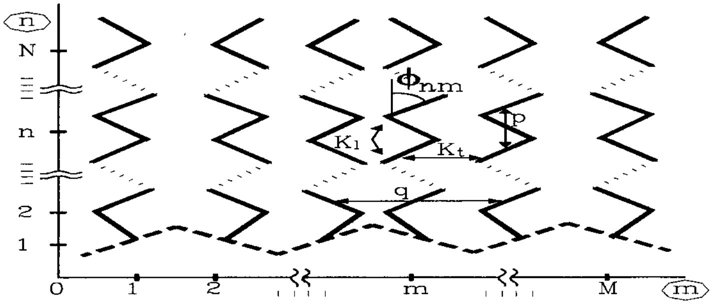


Figure 1. Two-dimensional domain, composed by M chains with N rigid elements with orientational interactions. The energetic constant K_l characterizes the bending rigidity of a chain, and K_t is the constant of interchain orientational interactions. The main chain is designated by the dashed line (by simulation of comb-shaped polymers). The parameters p and q characterize distances between elements of the given chain or different chains in the domain, accordingly.

In the low-temperature approximation the effective potential energy of intra-and interchain orientational nearest-neighbour interactions of chain elements – rotators, has the form [5]:

$$V_{ef}\{\varphi_{n,m}\} = \frac{1}{2}K_l \cdot \sum_{n,m}(\varphi_{n,m} - \varphi_{n-1,m})^2 + \frac{1}{2}K_t \cdot \sum_{n,m}(\varphi_{n,m} - \varphi_{n,m-1})^2 \tag{1}$$

The angle $\varphi_{n,m}$ determines an orientation of the n-th element in the m-th chain respect to a selected in the plane (n, m) direction (Fig. 1). The energetic constant K_l for polymer chains determines the mean cosine of angle between neighbouring chain elements, which is an important conformational characteristic of isolated semirigid chains ($K_t = 0$) (see ref.[2]). The value of K_l is related with the bending rigidity of a chain, characterized by a number of rigid elements in the statistical Kuhn segment with the length A. For very stiff chains $K_l \sim \frac{k_B T}{4} \cdot (A/l)$. The corresponding constant K_t describes interchain orientational interactions [4]. For anisotropic polymer sys-tems the relation $K_l >> K_t$ is usually valid.

In this paper three types of boundary conditions for chain ends are used: free, half-free and fixed ones.

1) «free ends»: $\varphi_{N+1,m} - \varphi_{N,m} = 0$, $\varphi_{1,m} - \varphi_{0,m} = 0$; (2a)

2) «half-free ends»: $\varphi_{N+1,m} - \varphi_{N,m} = 0$, $\varphi_{0,m} = 0$; (2b)

3) «fixed ends»: $\varphi_{N+1,m} = 0$, $\varphi_{0,m} = 0$. (2c)

In the frame of the given «orientational» model the boundary conditions «half-free ends» may be used by simulation of orientational order in the systems of comparatively short chains, orientated on a plane base or in dilute solutions of comb-shaped polymers. In last case at sufficiently strong interchain interactions of side mesogenic chains and small mobility of the main chains two-dimensional partly ordered structures may de formed spontaneously [12]. Rigid elements of side chains, bonded with the main chain (n = 1), have a restricted or fixed orientation, e.g. $\varphi_{0,m} = 0$, and in contrast, other ends of side chains (n = N) are «orientationally free» ones (Fig.1).

Intra-and interchain orientational order

The orientational correlation function are defined as the mean cosine of angle between chain elements [4–6]:

$$f(p,q) = \left\langle \cos(\varphi_{n+p,m+q} - \varphi_{n,m}) \right\rangle . \tag{3}$$

The integers p and q in Eq. (3) determine the number of elements between the considered chain elements in the longitudinal direction n, i.e. along chains, and in the transversal ones m, i.e. between chains, respectively (Fig. 1). By using the well-known method of normal modes [2] the orientational correlation function (3) for infinitely extended system ($N, M \to \infty$) is reduced to the form:

$$f(p,q) = \exp\left[-\frac{k_B T}{2} \int_0^{\pi}\int_0^{\pi} \frac{1 - \cos px \cos qy}{K_l (1 - \cos px) + K_t (1 - \cos qy)} dx dy \right] \tag{4}$$

The Eq. (4) may be represented [4] as power-low dependence

$$f(p,q) \cong \left(1 + \sqrt{\left(\frac{p}{p^*}\right)^2 + \left(\frac{q}{q^*}\right)^2} \right)^{-\gamma} , \tag{5}$$

where: the characteristical scale parameters $p^* = 1/\pi\sqrt{K_l/K_t}$ and $q^* = 1/\pi\sqrt{K_t/K_l}$.

The exponent γ in Eq. (5) is equal to the ratio of the energy of thermal motion ($k_B T$) to the geometric mean of intra- and interchain interactions energies of chain elements (K_l and K_t, accordingly)

$$\gamma = k_B T / 2\pi\sqrt{K_l K_t} . \tag{6}$$

The power law (5) is characteristic for asymptotic behaviour of orientational correlation functions in infinitely extended two-dimensional system with the "quasi-long-range" [11] order. This decay is slower than the exponential one for one-dimensional systems (e.g. a liner isolated chain with the nearest-neighbour interactions of chain elements [2]). On the other hand, a long-range order doesn't exist in two-dimensional extended systems, in distinction from corresponding three-dimensional systems. For sufficiently large, but finite values M and N, the orientational correlation function (4) is represented in the form:

$$f(p,q) \cong \exp\left[-\gamma \ln\left(1+\sqrt{\left(\frac{p}{p^*}\right)^2+\left(\frac{q}{q^*}\right)^2}\right)-\frac{k_B T}{2}\left(\frac{p}{K_l N}+\frac{q}{K_t M}\right)\right]. \tag{7}$$

Increasing dimensions of the domain ($M,N \to \infty$) the Eq. (7) transforms to the power law (5), characteristical for two-dimensional extended systems of long chains.

The correlation function (7) corresponds to the boundary conditions «free ends» because the exponent in Eq. (7) contains the terms $\frac{p}{K_l N}$ and $\frac{q}{K_t M}$. These terms are associated with the values of wave numbers $\psi_1 = 0$ and $\psi_2 = 0$ (see below Eq. (16), characteristical for the spectrum of normal modes for the most large-scale motions of chains in the longitudinal and transversal directions of the domain at «orientationally free» ends of the chains.

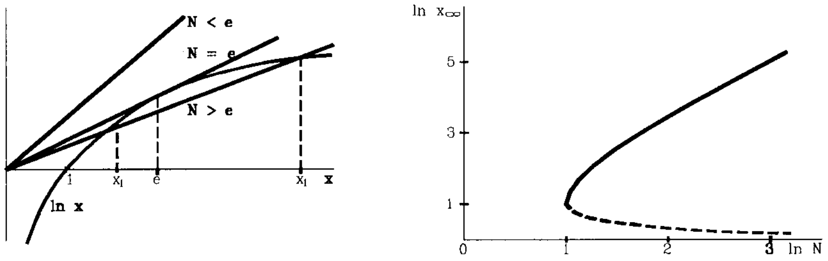
Analysis of Eq. (7) shows that correlations of orientations between two elements, disposed on the distance p (in the number on elements) along the same chain ($q = 0$) or elements, placed in different chains and separated by q chains (at $p = 0$), depend basically on the relation between p and the of the "height" of the domain (N), and on the relation between q the "width" of the domain (M), accordingly (Fig.1).

Ranges of values $p \le p_\infty(M)$ and $q \le q_\infty(N)$ exist, where the power low (5) is valid both for intra-and interchain orientational functions (accordingly, $f_{//}(p) = f(p, 0)$ and $f_{\perp}(q) = f(0, q)$) as before. The values $p_\infty(M)$ and $q_\infty(N)$, determining the boundaries of these ranges, may be obtained from a solution of transcendental solution: $x_\infty = x_0 \ln(1+x_\infty)$, where $x_\infty = p_\infty/p^*$ for $x_0 = N$ and $x_\infty = q_\infty/q^*$ for $x_0 = M$, accordingly (Fig. 2).

If the values of parameters p and q are beyond the indicated boundaries ($p > p_\infty$ or $q > q_\infty$), then correlations of orientations between elements of the given or different chains decrease by the exponential law:

$$f(r_\beta) \approx \exp\left(-\frac{r_\beta}{a_\beta}\right), \qquad \beta = \perp, \|, \qquad r_\| = p, \qquad r_\perp = q, \tag{8}$$

characteristic, correspondingly for isolated polymer chains or one-dimensional chain of rotators [2]. The quantity $a_\| = \frac{2K_\|}{k_B T} = aM$ determines an effective persistent length of the



a) b)

Figure 2. a) The graphical solution of the equationx $x_\infty = x_0 \ln(1+x_\infty)$, b) The solution x_∞ versus the number of chain elements N in the chain.

domain in the longitudinal direction n (along the chains), where $a = \frac{2K_l}{k_B T}$ is the dimensionless persistent length of isolated polymer chain. The correlation "memory" of the chain in the domain is retained over a length $a_{||}$. Therefore, conformational properties along the chains in the orientationally ordered two-dimensional multichain domain with a sufficiently large "height" ($N > p_c(M)$) resemble conformational properties of «thick» persistent chain with the modulus of elasticity $K_{//}$, corresponding to a bending of the domain as a whole. The quantity $K_{//}$ is equal the product of modulus of elasticity of isolated polymer chain K_l and the number M of chains in the domain, e.g. $K_{//} = K_l \cdot M$. Because of this, at large-scale bendings of such domain an individuality of a single macromolecule as a statistical ensemble, participating in a thermal motion, is lost, as it was supposed in many "bundle" and "domains" models of polymer systems [10]. The similar effect for flexible-chain polymers was determined clearly by De Gennes as: «We are standing together, and we are falling separately» [14].

The corresponding dimensionless parameter $a_\perp = \frac{2K_\perp}{k_B T} = bN$ is characteristical correlation length in the transversal direction of the domain (between elements of different chains). The effective constant of interchain interactions $K_\perp = K_t N$, determining the modulus of elasticity for splay deformation of the domain, increases with the elongation of the chains (N). This means that the boundary of manifestation of two-dimensional "quasi-long-range" [11] order q_∞ relegates in the range of large distances q between chains. Thus, the degree of the mutual lateral ordering increases with the increasing of the contour length of the chains (N). The similar effect manifests itself in experimental date on the optical anisotropy of poly-n-alkylmethacrylates [12]. A further elongation of the chains ($N \to \infty$) results to the replacing of the exponential law (8) of decrease of correlation between orientations of disposed elements on more slowly power law (5) that produces some larger orientational ordering of the chains in the domain.

Therefore, an interchain ordering in two-dimensional finite polymer systems (domains, bundles etc.) may be induced owing to both the increase of the constant of interchain interactions K_t, e.g. in consequence of more perfect packing of the chains themselves, like in infinitely extended systems [4], or owing to the elongation of the chains forming the domain (of course, at the given bending rigidity of the chains and later orientational interactions). Let us consider effect of these factors on parameters of orientational order and times of local motions in extended domains with sufficiently large number of chains ($M >> 1$), but with a finite contour length of the chain (N) – “stripes”.

Orientational order in “stripes”

Parameters of short- and long interchain orientational order μ and $\tilde{\mu}$ are defined as follows

$$\mu = \frac{1}{N-1}\sum_{n=2}^{N}\left\langle \cos(\varphi_{n,m} - \varphi_{n-1,m}) \right\rangle, \tag{9}$$

$$\tilde{\mu} = \frac{1}{N}\sum_{n=1}^{N}\left\langle \cos\varphi_{n,m} \right\rangle. \tag{10}$$

In this paper the quantities μ and $\tilde{\mu}$ are calculated by the method of normal modes [2] at different contour lengths of the chains (N) at the given bending rigidity and the value of interchain orientational interactions. In this method instead of angles $\varphi_{n,m}$ in Eq. (1) the normal coordinates $Q_{\psi_1\psi_2}$ are introduced

$$\varphi_{n,m} = \sum_{\psi_1\psi_2} A_{n,m}^{\psi_1\psi_2} \cdot Q_{\psi_1\psi_2}. \tag{11}$$

The coefficients $A_{n,m}^{\psi_1\psi_2}$ in Eq. (11) and values of the wave numbers ψ_1 and ψ_2 (the spectrum) depend on the type of boundary conditions [2]. The spectrums of ψ_1 have the form

$$\psi_1 = \frac{\pi(q-1)}{N}, \qquad \psi_1 = \frac{\pi q}{N+1}, \qquad \psi_1 = \frac{\pi(2q+1)}{2N+1}, \tag{12}$$

correspondingly for free, fixed and half-free boundary conditions (3), where $q = 1,\dots,N$. For infinitely extended domains (along the direction m on the Fig. 1, $M \to \infty$) – “stripes”, the spectrum of ψ_2 is continuous and arranged in the range of values from 0 to π.

The calculations show that at the given intra-and interchain interactions an elongation of the chains, forming the domain, results to a local ordering of chains (at free boundary conditions) or, on the contrary, to the decreasing of the parameter of short-range orientational order (at fixed and half-free boundary conditions, see Fig. 3). When the contour length of the chains (N) increases, independently of type of boundary conditions, all dependences μ (N) on Fig. 3 tend asymptotically to the limiting value

$$\mu_\infty = exp\left[-\frac{2}{\pi \cdot a}\, arcsin\sqrt{\frac{1}{1+\varepsilon}}\right];\quad \varepsilon = {}^{b}\!/_{a}. \tag{13}$$

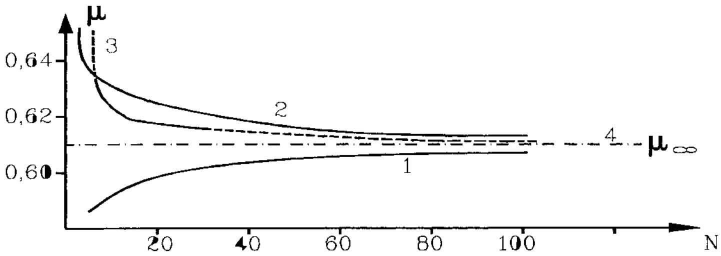


Figure 3. The parameter of short-range interchain orientational order μ versus the number N of rigid elements in the chain with the given bending rigidity ($a = 2K_l/k_BT = 1$) and the value of interchain orientational interactions ($b = 2K_t/k_BT = 1$) for free (1), half-free (2), and fixed (3) boundary conditions. The value μ_∞ characterizes a local interchain order in the corresponding infinitely extended system ($N = \infty$, dash-doted line 4).

The quantity μ_∞ corresponds to the order in infinitely extended systems of long chains ($N = \infty$) [7]. Its value is defined only by bending rigidity of the chains ($a = 2K_l/k_BT$) and the value of interchain orientational interactions ($b = 2K_t/k_BT$).

Independently of type of boundary conditions, the parameter of large- range orientational order tends to zero as the contour length of chains (N) increases (Fig. 4). This property corresponds to the general Mermin-Wagner theorem [15]. According to this theorem, the long-range order doesn't exist in one- or two-dimensional systems, where an energy of nearest-neihbouring interactions is in-variant under a continuous transformation group of symmetry, e.g. the group of rotations in the plane, like in this model with the potential energy (1) of intra- and interchain interactions.

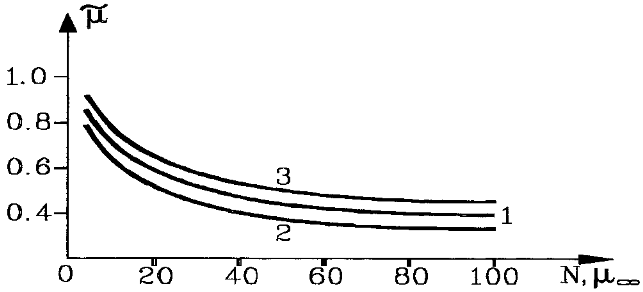


Figure 4. The parameter of long-range orientational order $\tilde\mu$ versus the number N of rigid elements in the chain with the given bending rigidity ($a = 2K_l/k_BT = 1$) and the value of interchain orientational interactions ($b = 2K_t/k_BT = 1$) for free (1), half-free (2), and fixed (3) boundary conditions. The line $\mu_\infty = 0$ corresponds to infinitely extended systems ($N = \infty$).

Equations of motion and local mobility

Equations of motion for the angles $\varphi_{\vec r}$ of chain elements are obtained on the base of methods applied in dynamic theory of individual chains [2]

$$\frac{d}{dt}\varphi_{\vec r}(t) + \sum_{\vec m} T_{\vec r,\vec r'}\frac{\partial V_{ef}}{\partial \varphi_{\vec r'}} = 0; \qquad \vec r = (n,m);\ \vec r' = (n',m'). \tag{14}$$

These equations are valid for comparatively short-scale, local relaxation processes, when the coefficients of the tensor of mobility $T_{\vec r,\vec r'}$ in Eq. (14) are independent neither of conformations nor of a scale of motion of chains in the domain

$$T_{\vec r,\vec r'} = (1/\zeta)\left(2\delta_{m,m'} - \delta_{n-1,n'} - \delta_{n+1,n'}\right)\cdot\delta_{m,m'}, \tag{15}$$

where ζ is the coefficient of local viscous friction of a chain element.

Then, the Eq. (14) are linear, and according to the method of normal modes [2] a solution of Eq. (14) is represented in the form

$$\varphi_{\vec n}(t) = \sum_{\vec\psi} e^{i\vec n\vec\psi}\cdot Q_{\psi_1\psi_2}\exp\left[-t/\tau(\vec\psi)\right], \tag{16}$$

where $Q_{\psi_1\psi_2}$ are normal coordinates with the components of a wave vector $\psi_1(0\le \psi_1 \ge \pi)$ and $\psi_2(0\le \psi_2 \ge \pi)$. The spectrum $\tau(\vec\psi)$ of relaxation times for local motions in Eq. (16) has the form

$$\frac{1}{\tau(\vec\psi)} = \frac{4(1-\cos\psi_1)}{\zeta}\left[K_1(1-\cos\psi_1) + K_2(1-\cos\psi_2)\right]. \tag{17}$$

The multiplier $(1-\cos\psi_1)$ in Eq. (17), as usually [2], came into being in consequence of kinematical bonds of elements in polymer chains that takes into account also in the structure of the tensor of mobility $T_{\vec{n},\vec{m}}$ in Eq. (15). The spectrum $\tau(\vec{\psi})$ in Eq. (17) allows to calculate the non-linear time dependences $P_1(t)=\left\langle\cos\left[\varphi_{\vec{n}}(t)-\varphi_{\vec{n}}(0)\right]\right\rangle$ and $P_2(t)=\left\langle\cos^2\left[\varphi_{\vec{n}}(t)-\varphi_{\vec{n}}(0)\right]\right\rangle-1$ of angles $\varphi_{\vec{n}}$ of chain elements. The correlation functions $P_1(t)$ and $P_2(t)$ characterize the mean cosine and the mean square of cosine of rotation angle of the given chain element in the time *t*, accordingly. These functions are used usually for description of local orientation dynamics [2, 16, 17] in experiments on dielectric relaxation (the function $P_1(t)$) and polarized luminescence, NMR, EPR etc. (the function $P_2(t)$). In the low-temperature approximation for the considered two-dimensional model there is the relation $P_2(t)=P_1{}^2(t)$ [4]. Thus, it suffices to investigate only the behaviour of time dependence $P_1(t)$.

The initial slope of the functions $P_1(t)$ and $P_2(t)$ is independent of the constants of intra-and interchain orientational K_l and K_t in Eq. (1), see Fig. 5.

$$\ln P_1(t)\approx-2\cdot D_0\cdot t, \qquad t\le\tau_{min}=\tau(\pi,\pi)=\zeta/16(K_l+K_t), \qquad D_0=k_B\cdot T/\zeta\,. \quad (18)$$

At large times the function $P_1(t)$, and consequently the function $P_2(t)$, decreases by the power law (Fig. 5)

$$P_1\approx(t^*/t)^{\gamma/4}, \qquad t\ge t^*=\zeta\cdot K_l\,/(K_l+K_t)^2, \quad (19)$$

where the parameter γ is defined in Eq. (6). Therefore, the function $P_1(t)$ decreases more slowly than the corresponding dependence

$$P_1(t)\approx exp(-\sqrt[4]{t/t_{ef}}), \qquad t\ge t_{ef}=\frac{\pi}{D_0}\cdot(K_l\,/k_B\cdot T)^3\,, \quad (20)$$

characteristic [2] for isolated chain ($\gamma=\infty$) with the coefficient of rotation diffusion D_0 of a chain element.

Relaxation times of local mobility of chain elements are defined from the decrease of the function $P_1(t)$ by a factor of *e*, lire that for exponential time functions [2]. The times of local motions rise and, correspondingly, intramolecular mobility diminishes essentially the with decrease of the parameter γ (Fig. 5), i.e. with increase of interchain orientational interactions (K_t) or bending rigidity of the chains (K_l), see Eq. (6). Inasmuch, as it is shown above, an increase of degree of mutual ordering in the domain may be realized owing to a elongation of

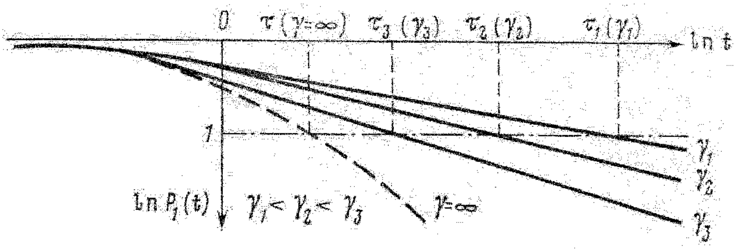


Figure 5. The time dependence of the mean cosine of rotation angle of the given rigid element $P_1(t)$ at different values of parameter γ. $\tau(\gamma)$ is the time of local motions. The line $\gamma = 0$ corresponds to an isolated semirigid chain ($N = \infty$).

chains (at fixed bending rigidity of the chains and the value of interchain orientational interactions), it is naturally to suppose that time of local motions must rise also, as the number of chain elements N increases. This may be one of effects resulting in slowing-down of local mobility in comb-shaped polymers with the ordering of side chains owing to the elongtation of chains [12]. Dielectric relaxation [16] and polarized luminescence [17] methods on the investigation of nano-scaled mobility ($\tau \sim 10 \div 30$ ns at $T = 300^0 K$) in the dilute melts of comb-shaped polymers of type PMA - n ($n = 4 \div 22$) provide quality support for this assumption.

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