Tension enhancement in branched macromolecules upon adhesion on a solid substrate

J. Paturej1,2(a), L. Kuban3, A. Milchev1,4 and T. A. Vilgis1

1 Max Planck Institute for Polymer Research - 10 Ackermannweg, 55128 Mainz, Germany, EU
2 Institute of Physics, University of Szczecin - Wielkopolska 15, 70451 Szczecin, Poland, EU
3 Institute of Thermal Machinery, Czestochowa University of Technology - Armii Krajowej 21 42200 Czestochowa, Poland, EU
4 Institute for Physical Chemistry, Bulgarian Academy of Sciences - 1113 Sofia, Bulgaria, EU

received 12 December 2011; accepted in final form 25 January 2012
published online 2 March 2012

PACS 82.37.-j – Single molecules kinetics
PACS 82.35.Lr – Physical properties of polymers
PACS 05.40.-a – Fluctuation phenomena, random processes, noise, and Brownian motion

Abstract – The effect of self-generated tension in the backbone of a bottle-brush (BB) macromolecule, adsorbed on an attractive surface, is studied by means of molecular-dynamics simulations of a coarse-grained bead-spring model in the good solvent regime. The BB molecule is modeled as a backbone chain of \(L\) beads, connected by breakable bonds and with side chains, tethered pairwise to each monomer of the backbone. Our investigation is focused on several key questions that determine the bond scission mechanism and the ensuing degradation kinetics: how are frequency of bond scission and self-induced tension distributed along the BB backbone at different grafting density \(\sigma_g\) of the side chains? How does tension \(f\) depend on the length of the side chains \(N\), and on the strength of surface adhesion \(\epsilon_s\)? We examine the monomer density distribution profiles across the BB backbone at different \(\epsilon_s\) and relate it to adsorption-induced morphological changes of the macromolecule whereby side chains partially desorb while the remaining chains spread better on the surface. Our simulation data are found to be in qualitative agreement with experimental results and recent theoretical predictions. Yet we demonstrate that the interval of parameter values where these predictions hold is limited in \(N\). Thus, at high values of \(\epsilon_s\), too long side chains mutually block each other and freeze effectively the bottle-brush molecule.

Copyright © EPLA, 2012

Introduction. – One of the most outstanding challenges in modern material sciences is the design and synthesis of “smart” macromolecules with stress-activated functions [1,2]. During the last decade one observes thus a rapidly escalating interest in the field of novel polymer mechanochemistry which, in contrast to the traditional (non-selective) one, allows to control bond tension on molecular length scales [1,3–5]. Examples related to these advances enable, for instance, rupture of specific chemical bonds [6,7], steering the course of chemical reactivity [8–11], changing color of materials [12] or mapping their stress distribution at molecular level [13,14].

In a series of recent experiments, a strong enhancement of the tension in the (typically, polymethacrylate with degree of polymerization \(L = 3600\)) backbone of bottle-brush polymers with side chains of poly(n-butyl acrylate) of length \(N = 140\), self-induced upon adsorption on a solid surface (mica), was reported [6,15–17]. An experimental method for control and manipulation of the bond cleavage in bottle-brush backbones was also proposed [17]. Thus, a selectivity of bond breakage can be achieved by tuning the molecular size of such macromolecules which makes it possible to fabricate the brush so as to focus tension in the middle of the molecule.

The increase of the bond tension in these macromolecules is induced by the steric repulsion of the side chains as they tend to maximize the number of contacts with the substrate in order to gain energy. This tension, which depends on grafting density \(\sigma_g\), on the side chain length \(N\), and on the strength of substrate attraction \(\epsilon_s\), effectively
lowers the energy barrier for bond scission. As observed in experiments, self-induced build-up of tension proves sufficient to instantly sever covalent bond in the backbone.

The possibility for breaking strong covalent bonds is also an interesting problem from the standpoint of fundamental physics. Amplification of tension in branched polymers has been considered theoretically by Panyukov and collaborators in several recent works [18–20] by means of scaling theory and self-consistent field techniques. Numerous possible regimes of brush-molecule behavior in terms of \( N, \sigma_g \) and \( \epsilon_s \) have been outlined [18]. It was argued that polymers with branched morphology, physically adsorbed on an attractive plane, allow focusing of the side chain tension on the backbone whereby at given temperature \( T \) the tension in the backbone becomes proportional to the length of the side chain, \( f \approx f_\Sigma N \). Here \( f_\Sigma \) denotes the maximum tension in the side chains, \( f_\Sigma \approx k_B T / b \), with \( k_B \) being the Boltzmann constant, and \( b \) the Kuhn length (or, the monomer diameter for absolutely flexible chains).

However, a comprehensive understanding of covalent bond breaking in adsorbed branched polymers still has to be reached. Many of the detailed theoretical predictions can hardly be measured directly experimentally. It remains unclear how exactly tension builds up with growing adhesion to the solid surface and impact exercise side chain length \( N \) and grafting density \( \sigma_g \) on this phenomenon. Much insight in this respect can be provided by computer experiments, yet there have been only few such studies [18,21] which did not focus on these questions.

In an earlier molecular-dynamics (MD) simulation study of the scission kinetics it was found that mean lifetime of a bond becomes more than an order of magnitude shorter when the bottle-brush molecule spreads on an adhesive surface [21]. These simulation results [21] indicated also that the probability distribution for bond scission along the backbone of a bottle brush is sensitive to the grafting density (and, therefore, to the degree of steric repulsion) of the side chains. The shape of this distribution resembles the experimentally established one [15] only for weaker repulsion when the side chains are short and do not mutually block one another.

In this letter we report our MD results on the first direct measurement of the adsorption-induced tension \( f \) in the backbone of a bottle-brush macromolecule whereby we examine the influence of varying parameters: grafting density \( \sigma_g \), adsorption strength \( \epsilon_s / k_B T \) as well as the length of side chains \( N \) on the resulting increase of \( f \).

**The model.** We consider a three-dimensional coarse-grained model of a bottle-brush macromolecule which consists \( L \) monomers in the backbone connected by bonds. Moreover, two side chains of length \( N \) are grafted to every \( \sigma_g \)-th repeatable unit of the backbone (except for the terminal beads of the backbone where there are three side chains anchored). In this way a grafting density \( \sigma_g \), which gives the number of side chains pairs per unit length, is defined. Thus, the total number of monomers in \( M \) the brush molecule is \( M = L + 2N(L - 1)\sigma_g + 2 \).

The bonded interaction of each segment in the brush with its neighbors is described by the frequently used Kremer-Grest potential, \( V^{KG}(r) = V^{FENE} + V^{WCA} \), with the so-called "finely-extensible nonlinear elastic" (FENE) potential:

\[
V^{FENE}(r) = -0.5k_B T \ln[1 - (r/r_0)^2],
\]

and the Weeks-Chandler-Anderson (WCA) (i.e., the shifted and truncated repulsive branch of the Lennard-Jones potential) given by:

\[
V^{WCA}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 + \frac{1}{4} \right] \theta(2^{1/6}\sigma - r).
\]

In eq. (1) \( k = 30, r_0 = 1.5 \) whereas in eq. (2) one has \( \theta(x) = 0 \) or 1 for \( x < 0 \) or \( x \geq 0 \), and \( \epsilon = 1, \sigma = 1 \). The potential \( V^{KG}(r) \) has a minimum at bond length \( r_{\text{bond}} \approx 0.96 \). Thus, the bonded interaction, \( V^{KG}(r) \), makes the bonds of the brush in our model unbreakable which is convenient when measuring bond tension is our main concern. In the course of the study, however, we have also analyzed the case when "backbone" bonds may undergo thermal scission. The bonded potential for the "backbone" monomers is then replaced by \( V^b(r) = V^M + V^{WCA} \), with a Morse potential

\[
V^M(r) = D\left[ 1 - \exp\left[-\alpha(r - b)\right] \right]^2
\]

which was recently used in simulations exploring breaking of polymer chains [22–24] and bottle brushes [21]. In eq. (3) \( \alpha \) is a constant that determines bond elasticity, we use here \( \alpha = 1 \). The dissociation energy \( D \) of a given bond is measured in units of \( k_B T \), where \( k_B \) is the Boltzmann constant and \( T \) denotes the temperature. We use here \( D = 1 \). The monomer diameter in the case of "breakable" potential (3) is \( b = 2^{1/6}\sigma \approx 1.12r \). All non-bonded interactions between monomers are taken into account by means of the WCA potential, eq. (2). As a consequence, the interactions in our model correspond to good solvent conditions.

The substrate in the present investigation is considered simply as a structureless adsorbing plane, with a Lennard-Jones potential acting with strength \( \epsilon_s \) in the perpendicular z-direction, \( V^{LJ}(z) = 4\epsilon_s [(\sigma/z)^{12} - (\sigma/z)^6] \). In our simulations we consider as a rule the case of strong adsorption, \( \epsilon_s / k_B T = 4.0–8.0 \). With these interaction between the monomers, and at different degree of adhesion to the surface, we observe well equilibrated bottle-brush molecules, as shown in fig. 1.

In reality the thermal energy is \( k_B T \approx 4.11 \times 10^{-21} \) J at absolute temperature \( T \approx 300 \) K, so for a typical Kuhn length of \( \sigma = 1 \) nm one obtains for the tension \( f \approx 4 \) pN. Estimates show [20] that this tension is too small to significantly change the lifetime \( \tau \approx 10^{10} \) of covalent bonds with energy \( \approx 100k_B T \). Adsorbed bottle-brush molecules on graphite or water/ethanol mixtures with spreading...
Tension enhancement in branched macromolecules

Fig. 1: (Color online) Snapshots of equilibrated bottle brushes with $L = 121$ backbone monomers and 244 side chains of length $N = 30$ ($\sigma_g = 1$) displayed for different adsorption strengths: (a) $\epsilon_s/k_B T = 0$, (b) $\epsilon_s/k_B T = 4.0$, and (c) $\epsilon_s/k_B T = 8.0$. The spreading of the BB molecule on the surface is clearly observed while adhesion $\epsilon_s/k_B T$ grows.

The spreading of the BB molecule on the surface is clearly observed while adhesion $\epsilon_s/k_B T$ grows.

The spreading of the BB molecule on the surface is clearly observed while adhesion $\epsilon_s/k_B T$ grows.

Fig. 2: (Color online) Starting configuration of a bottle-brush molecule (a "centipede") with $L = 13$ (backbone) and $N = 3$ (side chain), so that for a grafting density $\sigma_g = 1$, the total number of segments $M = 97$, and for $\sigma_g = 1/4$, one has $M = 43$.

The bottle-brush dynamics is obtained by solving a Langevin equation for the position $q_n = [x_n, y_n, z_n]$ of each bead in the molecule,

$$m\ddot{q}_n = F_j^n + F_{\text{WCA}}^n - \gamma \dot{q}_n + R_n(t), \quad (n, \ldots, N), \quad (4)$$

which describes the Brownian motion of a set of bonded particles. In eq. (4) we choose the force $F_j^n$ with $j = M$, or KG, depending on the character of bonded (breakable, eq. (3)) or non-breakable, eq. (1)) interaction. The influence of solvent is split into slowly evolving viscous force and rapidly fluctuating stochastic force. The random, Gaussian force $R_n$ is related to friction coefficient $\gamma$ by the fluctuation-dissipation theorem, $\gamma = 0.25$. The integration step is 0.002 t.u. Time is measured in units of $\sqrt{m\sigma^2/D}$ or $\sqrt{m\sigma^2/\epsilon}$ (where $m$ denotes the mass of the beads, $m = 1$), depending on whether $V^{KG}(r)$ or $V^{M}$ is used. We emphasize at this point that in our coarse-grained model no explicit solvent particles are included. Our simulation was performed in the weakly damped regime of $\gamma = 0.25$ as we modeled the interface between solid substrate and air. However, we carried out also simulation in the strongly damped regime for $\gamma = 10$. No qualitative changes were discovered except an absolute overall increase of the rupture times which is natural for a more viscous environment.

The initially created configurations, fig. 2, are equilibrated by MD for a sufficiently long period of time so that the mean squared displacement of the polymer center-of-mass moves a distance several (3-5) times larger than the polymer size. We then start the simulation with a well-equilibrated conformation —fig. 3— and measure the tension $f$ generated by the steric repulsion of side chains.
on the covalent bonds that comprise the macromolecule backbone. Tension was measured by sampling the length of each bond and using derivative of eq. (1). In separate runs we allow thermal scission of bonds by using the second bonded potential given by eq. (3). In that case we sample the frequency of bond breaking with respect to the bond position in the backbone and create a probability distribution (a rupture probability histogram).

**MD results.** – An important aspect of the tension-induced scission of bonds in a BB molecule, adsorbed on a solid plane is the probability distribution of rupture (scission frequency) along the molecule backbone since it determines the fragmentation kinetics which can be experimentally analyzed. In order to interpret experimental results [16,17] by means of scaling theory [15,18], one assumes that tension of the side chains is focused onto the backbone at its ends and transmitted through the middle part of the backbone. This would then lead to uniform scission probability of each bonds along the backbone. In fig. 4 we demonstrate that the rupture frequency depends, in fact, essentially on the side chain length, \( N \), provided grafting density \( \sigma_g \) is held constant (in an earlier paper we found that this frequency does not depend on backbone length \( L \) for sufficiently long BB molecules [21]). While the rupture frequency levels off and stays uniform in the middle for \( \sigma_g = 1 \) and \( N = 1 \), cf. upper left panel in fig. 4, one observes sharp focusing at both ends of the chain for \( N = 5 \). As argued in ref. [21], this effect is due to mutual blocking of the side chains which are in the middle of bottle-brush molecule. In contrast, side chains that are closer to the ends of the backbone are much more mobile and, therefore, pull on the backbone more frequently. Thus, it is not only the tension value but also the rate at which this tension is applied that determine eventually the distribution of scission rates along the backbone. However, for \( N = 5 \) and \( \sigma_g = 1/2 \) the distribution changes qualitatively, and attains a shape as for \( \sigma_g = 1.0, N = 1 \) again. Moreover, for smaller density of grafting, \( \sigma_g = 1/6 \), one finds “comb-like” distribution which suggests that bonds adjacent to the tethered backbone monomers break then five times more frequently.

The distribution of tension \( f \) for different values of the governing parameters \( \epsilon_s, \sigma_g \) and \( N \), is shown in figs. 5(a), (b), (c). Evidently, \( f \) reaches a plateau away from chain ends. From fig. 5(d), the mean value \( \langle f \rangle \) is found to grow steadily with adsorption strength, \( \epsilon_s \) (for \( \sigma_g = 1 \)), and also with grafting density, \( \sigma_g \) (for \( \epsilon_s/k_BT = 8 \)). Our simulation results yield a Gaussian distribution of \( f \) around its mean value \( \langle f \rangle \) (not shown here). The tension is seen to focus on the middle of the chain with increasing side chain length —fig. 5(c). One should note again the comb-like variation

---

**Fig. 4:** (Color online) Rupture probability histograms for a polymer backbone with \( L = 61 \) presented for different values of grafting density \( \sigma_g \) and length of side chains \( N \) as indicated. Here \( \epsilon_s/k_BT = 4.0 \) and the bonded interaction is governed by Morse potential given by eq. (3).

**Fig. 5:** (Color online) The tension profile along the brush backbones made of \( L = 61 \) particles displayed as indicated for different: (a) adsorption strengths \( \epsilon_s/k_BT \), (b) grafting densities \( \sigma_g \), (c) lengths of side chains \( N \). (d) Variation of the mean tension \( \langle f \rangle / \langle f_0 \rangle \) (in dimensionless units) generated in the backbone of bottle brush with \( L = 121 \) as a function of adsorption strength \( \epsilon_s/k_BT \) and grafting density \( \sigma_g \) (inset).
of $f$ over the successive bonds at $\sigma_g = 1/6$, i.e. exactly where the side chains are grafted.

In fig. 6 we show one of the main results of this study — the variation of tension in the bonds along the bottle-brush backbone with growing length $N$ of the side chains whereby both the adsorption strength, $\epsilon_s$, as well as the grafting density $\sigma_g$ are varied. In all cases $f$ is displayed in dimensionless units, taken as the ratio to mean bond tension of a non-adsorbed BB molecule $f_0$. Evidently, the theoretical predictions [18] for a linear scaling relationship, $f \propto N$, appears only for rather short side chains, $N < 10$ at the largest density $\sigma_g = 1$ and adsorption strength $\epsilon_s = 8.0$ while for weaker adhesion, $\epsilon_s = 4.0$, one finds $f \propto N^{1/4}$, as predicted [18], yet only for $10 \leq N \leq 60$. For loosely grafted side chains, $\sigma_g \leq 0.5$ and weaker adsorption, $\epsilon_s = 2.0$, the tension becomes progressively insensitive to $N$, saturating at a constant value at shorter and shorter length of the side chains. At $\sigma_g = 1/6$ the tension $f$ remains unaffected by adsorption whatsoever for any $N$.

Fig. 6: (Color online) (a)–(c) Mean (dimensionless) tension ($f$) in a bottle-brush backbone composed of $L = 121$ particles is plotted as a function of the number of beads in the side chains $N$ for different adsorption strengths $\epsilon_s/k_BT$ (as indicated), and grafting density: (a) $\sigma_g = 1$, (b) $\sigma_g = 1/2$, (c) $\sigma_g = 1/6$. Dashed lines represent linear fits with different slope.

Generally, one observes progressive deviations from a power-law relationship for longer side chains $N > 70$ even at the strongest adhesion. We believe that this is due to a progressive immobilization of the BB molecule for long side chains which spread nearly parallel to one another, cf. fig. 1, and mutually block each others mobility at large values of $\epsilon_s$, effectively “freezing” the macromolecule.

Finally, we show the density profile of all BB monomers in direction perpendicular to the backbone for several strengths of the adsorption potential — fig. 7. The shape of such cross-section profiles is important because it has been measured experimentally by AFM for poly(n-butyl acrylate) side chains on mica (for strong adsorption and $\sigma_g = 1$), and has also been reproduced by self-consistent field theory [18]. A close inspection of the cross-section profiles, shown in fig. 7, reveals qualitatively the same shapes as predicted theoretically [18]: i) for weak adsorption, $\epsilon_s/k_BT = 2.0$, one observes a nearly triangular “tent-like” profile; ii) for moderate adhesion, $\epsilon_s/k_BT = 4.0$, a shoulder of monolayer height is seen to form while most of the monomers still stay in the cap, and iii), at the strongest attraction, $\epsilon_s/k_BT = 8.0$, one finds a well-expressed monolayer and a narrow sharp cap (a cusp). Instead of a cusp right above the molecule backbone, however, the AFM experiment yields a well-defined parabolic maximum [19]. This is most probably due to the deformation of the BB cap by the AFM cantilever (about 20% of its height [18]) which thus modifies and distorts its true morphology. In fact, the sharp cusp-like cap is formed by partitioning of side chains into adsorbed and non-adsorbed ones at high grafting density — fig. 1(b), (c). Indeed, some of the side chains may relieve the deformation in the strongly adsorbed monolayer and minimize the BB free energy by

Fig. 7: (Color online) Monomer density profiles measured perpendicular to the backbone of bottle brushes with $L = 121$ and $N = 30$ displayed for different adsorption strengths as indicated in the legend. The inset presents the average number of chains above the substrate for a brush with $L = 61$ as a function side chain length $N$ for different sets of $\epsilon_s/k_BT$ and $\sigma_g$ (triangles stand for $\epsilon_s/k_BT = 1$ and $\sigma_g = 1/2$).
lifting off the substrate. In the inset to fig. 7 one may see the variation in the number of such off-chains with length \( N \) at different degrees of adhesion. For strong adsorption, \( \epsilon_s / k_B T = 8.0 \), the number of off-chains decreases with \( N \) since the energetic cost of desorption becomes too high. One can also see that for \( \sigma_g = 1/2, N_s = 1.0 \) the number of off-chains is close to zero since no crowding of monomers on the surface takes place. It should be clear that these “dangling” off-chains bring about the sharp cap in the cross-section density profile, observed in fig. 7.

**Concluding remarks.** – In this letter we report on simulation results from our study of bottle-brush macromolecules adsorbed on a structureless attractive surface and examine conditions which govern the build-up of bond tension and the ensuing frequency of bond scission distribution along the molecule backbone. Results are compared to those derived from experiments and theoretical considerations. Our findings can be summarized as follows:

- The variation of bond tension \( f \) with growing length of the side chains \( N \), adhesion strength \( \epsilon_s \), and grafting density \( \sigma_g \) comply with some important theoretical predictions [18] albeit in a rather narrow interval. Especially, a scaling law \( f \propto f_0 N^{1/4} \) in agreement with theory [18], yet for \( N < 70 \). Further increase of \( N \) slows down the tension build-up and eventually makes \( f \) insensitive to \( N \) as the side chains mutually block each other and the brush molecule gets progressively “frozen”.

- The distribution of tension and the scission frequency along the bonds of the bottle-brush backbone change strongly with \( N \) and \( \sigma_g \). Different combinations of these parameters can induce uniform, comb-like, or strongly focused tension distribution in adsorbed BB polymers.

- The cross-section monomer density profile of adsorbed bottle-brush molecules agrees with experimental observations and theoretical predictions of the shape at different regimes of adsorption. We find, however, the existence of sharp cusp-like peak in the profiles which manifests side chain partitioning into adsorbed and off-surface chains at strong adhesions and large grafting density.

***

We thank V. G. Rostiashvili for fruitful discussions. AM gratefully acknowledges support by the Max-Planck-Institute for Polymer Research in Mainz during the time of this investigation. This research has been supported by the Deutsche Forschungsgemeinschaft (DFG), Grants SFB 625/B4 and FOR 597.

**REFERENCES**

[1] CARUSO M. M., DAVIS D. A., SHEN Q., ODOM S. A., SOTTOS N. R., WHITE S. R. and MOORE J., Chemical Rev., **109** (2009) 5755.

[2] BLACK A. L., LENHARDT J. M. and CRAIG S. L., J. Mater. Chem., **21** (2011) 1655.

[3] BEYER M. K. and CLAUSEN-SCHAUMANN H., Chem. Rev., **105** (2005) 2921.

[4] LIANG J. and FERNÁNDEZ J. M., ACS Nano, **3** (2009) 1628.

[5] HUANG Z. and BOULATOV R., Chem. Soc. Rev., **40** (2011) 2359.

[6] PARK I., SHEIKO S. S., NSEE A. and MATYJASZEWSKI K., Macromolecules, **42** (2009) 1805.

[7] YANG Q.-Z., HUANG Z., KUCHARSKI T. J., KIVOSTTICHENKO D., CHEN J. and BOULATOV R., Nat. Nanotechnol., **4** (2009) 302.

[8] WHITA A. P., AINAVAPRU S. R. K., HUANG H. H. and FERNÁNDEZ J. M., Proc. Natl. Acad. Sci. U.S.A., **103** (2006) 7222.

[9] HICKENBOTH C. R., MOORE J. S., WHITE S. R., SOTTOS N. R., BAUDRY J. and WILSON S. R., Nature, **446** (2007) 423.

[10] LENHARDT J. M., BLACK A. L. and CRAIG S. L., J. Am. Chem. Soc., **131** (2009) 10818.

[11] LI Y., NSEE A., LEBEDEVA N. V., DAVIS T., MATYJASZEWSKI K. and SHEIKO S. S., J. Am. Chem. Soc., **133** (2011) 17479.

[12] DAVIS D. A., HAMILTON A., YANG J., CREAM L. D., VAN GOUGH D., POTISEK S. L., ONG M. T., BRAUN P. V., MARTINEZ T. J., WHITE S. R., MOORE J. S. and SOTTOS N. R., Nature, **459** (2009) 68.

[13] CHO S.-Y., KIM J.-G. and CHUNG C.-M., Sens. Actuators B, **134** (2008) 822.

[14] BRUNS N., PUSTELNY K., BERGERON L. M., WHITEHEAD T. A. and CLARK D. S., Angew. Chem., Int. Ed., **48** (2009) 5666.

[15] SHEIKO S. S., SUN F. C., RANDALL A., SHRVANYANTS D., RUBINSTEIN M., LEE H.-I. and MATYJASZEWSKI K., Nat. Lett., **440** (2006) 191.

[16] LEBEDEVA N. V., SUN F. C., LEE H.-I., MATYJASZEWSKI K. and SHEIKO S. S., J. Am. Chem. Soc., **130** (2007) 4228.

[17] PARK I., NSEE A., PIETRASKI J., MATYJASZEWSKI K. and SHEIKO S. S., J. Mater. Chem., **21** (2011) 8448.

[18] PANUKOV S., ZHULINA E. B., SHEIKO S. S., RANDALL G. C., BROCK J. and RUBINSTEIN M., J. Chem. Phys. B, **113** (2009) 3750.

[19] PANUKOV S., SHEIKO S. S. and RUBINSTEIN M., Phys. Rev. Lett., **102** (2009) 148301.

[20] SHEIKO S. S., PANUKOV S. and RUBINSTEIN M., Macromolecules, **44** (2011) 4520.

[21] MILCHEV A., PATUREJ J., ROSTIAISHVILI V. G. and VILGIS T. A., Macromolecules, **44** (2011) 3981.

[22] GHOSH A., DIMITROV D. I., ROSTIAISHVILI V. G., MILCHEV A. and VILGIS T. A., J. Chem. Phys., **132** (2010) 204902.

[23] PATUREJ J., MILCHEV A., ROSTIAISHVILI V. G. and VILGIS T. A., J. Chem. Phys., **134** (2011) 224901.

[24] PATUREJ J., MILCHEV A., ROSTIAISHVILI V. G. and VILGIS T. A., EPL, **94** (2011) 48003.