Thermal Degradation of Adsorbed Bottle-Brush Macromolecules: A Molecular Dynamics Simulation

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Abstract

The scission kinetics of bottle-brush molecules in solution and on an adhesive substrate is modeled by means of Molecular Dynamics simulation with Langevin thermostat. Our macromolecules comprise a long flexible polymer backbone with L segments, consisting of breakable bonds, along with two side chains of length N, tethered to each segment of the backbone. In agreement with recent experiments and theoretical predictions, we find that bond cleavage is significantly enhanced on a strongly attractive substrate even though the chemical nature of the bonds remains thereby unchanged.

We find that the mean bond life time $\langle \tau \rangle$ decreases upon adsorption by more than an order of magnitude even for brush molecules with comparatively short side chains $N = 1 \div 4$. The distribution of scission probability along the bonds of the backbone is found to be rather sensitive regarding the interplay between length and grafting density of side chains. The life time $\langle \tau \rangle$ declines with growing contour length L as $\langle \tau \rangle \propto L^{-0.17}$, and with side chain length as $\langle \tau \rangle \propto N^{-0.53}$. The probability distribution of fragment lengths at different times agrees well with experimental observations. The variation of the mean length $L(t)$ of the fragments with elapsed time confirms the notion of the thermal degradation process as a first order reaction.

1 Introduction

The study of degradation and stabilization of polymers is important both from practical and theoretical viewpoints [1]. Disposal of plastic wastes has grown rapidly to a world problem so that increasing environmental concerns have prompted researchers to investigate plastics recycling by degradation as an alternative [2]. On the other hand, degradation of polymers in different environment is a major limiting factor in their application. Recently, with the advent of exploiting biopolymers as functional materials [3, 4], the stability of such materials has become an issue of primary concern.

Most theoretical investigations of polymer degradation have focused so far on determining the rate of change of average molecular weight [5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. The main assumptions

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of the theory are that each link in a long chain molecule has equal strength and equal accessibility, that they are broken at random, and that the probability of rupture is proportional to the number of links present. Experimental studies of polystyrene, however, have revealed discrepancies [6] with the theory [5] so, for example, the thermal degradation stops completely or slows down markedly when a certain chain length is reached. Only few theoretic studies [15, 16] have recently explored how does the single polymer chain dynamics affect the resulting bond rupture probability. In both studies, however, for the sake of theoretical tractability one has worked with a model of a Gaussian chain bonded by linear (harmonic) forces whereby the anharmonic (non-linear) nature of the bonding interactions was not taken into account. One could claim that the process of thermal degradation still remains insufficiently studied and understood.

Meanwhile, recently it was found experimentally [17, 18, 19] that covalent bonds may spontaneously break upon adsorption of brush-like macromolecules onto a substrate. One studied brushes consisting of a poly(2-hydroxyethyl metacrylate) backbone and a poly(N-butyl acrylate) (PAB) side chains with degrees of polymerization $L = 2150 \pm 100$ and $N = 140 \pm 5$, and found spontaneous rupture of covalent bonds (which are otherwise hard to break) upon adsorption of these molecules on mica, graphite, or water-propanol interfaces [17]. As the densely grafted side chains adsorb, they experience steric repulsion due to monomer crowding which creates tension in the backbone. This tension, which depends on the grafting density, the side chain length, and the extent of substrate attraction, effectively lowers the energy barrier for dissociation, decreasing the bond life time [20]. Thus, one may observe amplification of bond tension from the pico-newton to nano-newton range which facilitates thermal degradation considerably.

Also recently, in several works Panyukov and collaborators [21, 22] predicted and theoretically described the effect of tension amplification in branched macromolecules. They argued that the brush-like architecture allows focusing of the side chain tension to the backbone whereby at given temperature T the tension in the backbone becomes proportional to the length of the side chain, $f \approx f_0 N$ [21, 22]. The maximum tension in the side chains is $f_0 \approx k_B T / b$ with k_B -being the Boltzmann constant, and b - the Kuhn length (or, the monomer diameter for absolutely flexible chains).

The effect of adsorption-induced bond scission might have important implication for surface chemistry, in general, and for specific applications of new macro- and supramolecular materials, in particular, for example, by steering the course of chemical reactions. One may use adsorption as a convenient way to exceed the strength of covalent bonds and invoke irreversible fracture of macro-molecules, holding the key to making molecular (DNA) architectures that undergo well-defined fragmentation upon adsorption.

In the present investigation we explore the process of chain fragmentation in desorbed and ad-sorbed bottle-brush macromolecules by means of a coarse-grained bead-spring model and Langevin dynamics. In Section 2 we describe briefly our model and then present our simulation results in Section 3. A summary of our results and conclusions is presented in Section 4. Anticipating, one might claim that the reported results appear in good agreement with observations and theoretical predictions.

2 The Model

We consider a $3d$ coarse-grained model of a polymer chain which consists of L repeatable units (monomers) connected by bonds, whereby each bond of length b is described by a Morse potential,

$$U_M(r) = D\{1 - \exp[-\alpha(r - b)]\}^2 \tag{1}$$

with a parameter $\alpha \equiv 1$. The dissociation energy of such bonds is D, measured in units of $k_B T$, where k_B denotes the Boltzmann constant and T is the temperature. The maximum restoring force of the Morse potential, $f_{max} = -dU_M/dr = \alpha D/2$, is reached at the inflection point, $r = b + \alpha^{-1} \ln(2)$. This force f_{max} determines the tensile strength of the chain. Since the bond extension $r - b$ between nearest-neighbor monomers along the polymer backbone in our $3d$-model is always positive, the Morse potential Eq. (1) is only weakly repulsive and segments could partially penetrate one another at $r < b$. Therefore, in order to allow properly for the *excluded volume* interactions between bonded monomers, we take the bond potential as a sum of $U_M(r)$ *and* the so called Weeks-Chandler-Anderson (WCA) potential, $U_{WCA}(r)$, (i.e., the shifted and truncated repulsive branch of

the Lennard-Jones potential);

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

with $\Theta(x) = 0$ or 1 for $x < 0$ or $x \geq 0$, and $\epsilon = 1$. The non-bonded interactions between monomers are also taken into account by means of the WCA potential, Eq. (2). Thus the interactions in our model correspond to good solvent conditions. The length scale is set by the parameter $\sigma = 1$ whereby the monomer diameter $b = 2^{1/6}\sigma \approx 1.12\sigma$.

In our MD simulation we use a Langevin equation, which describes the Brownian motion of a set of interacting particles whereby the action of the solvent is split into slowly evolving viscous force and a rapidly fluctuating stochastic force:

$$m \overrightarrow{v}_i(t) = -\zeta \vec{v}_i + \vec{F}^i_M(t) + \vec{F}^i_{WCA}(t) + \vec{R}^i(t).$$ (3)

The random force which represents the incessant collisions of the monomers with the solvent molecules satisfy the fluctuation-dissipation theorem $\langle R^i_\alpha(t) R^j_\beta(t') \rangle = 2\zeta k_B T \delta_{ij} \delta_{\alpha\beta} \delta(t - t')$. The friction coefficient ζ of the Langevin thermostat, used for equilibration, has been set at 0.25. The integration step is 0.002 time units (t.u.) and time is measured in units of $\sqrt{m/\sigma^2 D}$ where m denotes the mass of the beads, $m = 1$. We emphasize at this point that in our coarse-grained modeling no explicit solvent particles are included.
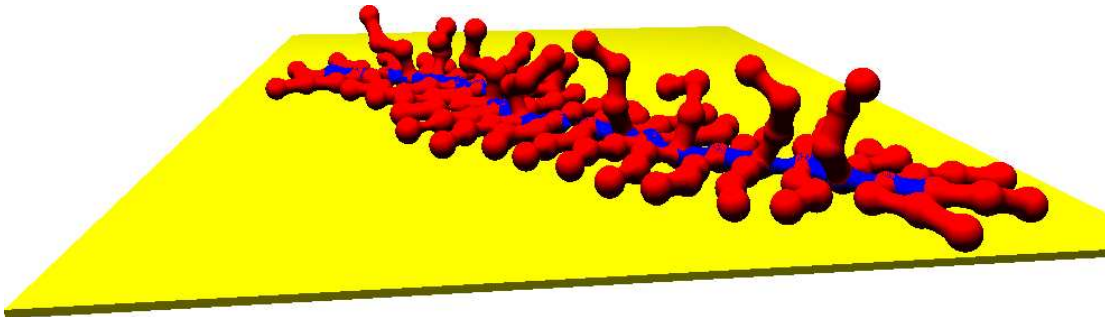

Figure 1: A snapshot of a bottle-brush molecule (a "centipede") with $L = 20$ backbone monomers (blue) and 122 side chains (red) of length $N = 4$. Here $k_B T = 1$ and strength of adsorption $\epsilon_s = 9.5$. Side chains which are too strongly squeezed by the neighbors are seen occasionally to get off the substrate in order to minimize free energy.

Two side chains of length N are tethered to *each* repeatable unit of the backbone except for the terminal beads of the polymer backbone where a single side chains is anchored only. Thus the total

number of monomers in the bottle-brush macromolecule is $M = L + 2N(L + 1)$. Because of the high grafting density, we use rather short side chains $N = 1 \div 5$ in our simulations - Fig. 1.

For the bonded interaction in the side chains we take the frequently used Kremer-Grest potential, $U_{KG}(r) = U_{WCA}(r) + U_{FENE}(r)$, with the so-called 'finitely-extensible non-linear elastic' (FENE) potential,

$$U_{FENE}(r) = -\frac{1}{2}kr_0^2 \ln\left[1 - \left(\frac{r}{r_0}\right)^2\right].$$ (4)

In Eq. (4) $k = 30$, $r_0 = 1.5$, so that the total potential $U_{KG}(r)$ has a minimum at bond length $r_{bond} \approx 0.96$. Thus, the bonded interaction, $U_{KG}(r)$, makes the bonds of the side chains in our model unbreakable whereas those of the backbone may and do undergo scission.

The substrate in the present study is considered simply as a structureless adsorbing plane, with a Lennard-Jones potential acting with strength ϵ_s in the perpendicular $z-$direction. In our simulations we consider as a rule the case of *strong* adsorption, $\epsilon_s/k_BT = 5.0 \div 10.0$.

We start the simulation with a well equilibrated conformation of the chain and examine the thermal scission of the bonds. We measure the mean life time τ until the first bond rupture occurs, and average these times over more than 2×10^4 events so as to determine the mean $\langle\tau\rangle$ which is also referred to as Mean First Breakage Time (MFBT). In the course of the simulation we also sample the probability distribution of bond breaking regarding their position in the chain (a rupture probability histogram), the probability distribution of the First Breakage Time, τ, as well as other quantities of interest. At periodic intervals we analyze the length distribution of backbone fragments and establish the Probability Distribution Function (PDF) of fragment sizes, $P(n,t)$, which also yields the time evolution of the mean fragment length $L(t)$.

Since in the problem of thermal degradation there is no external force acting on the chain ends, a well defined activation barrier for a bond scission is actually missing, in contrast to the case of applied tensile force. Therefore, a definition of an unambiguous criterion for bond breakage is not self-evident. Moreover, depending on the degree of stretching, bonds may break and then recombine again. Therefore, in our numeric experiments we use a sufficiently large expansion of the bond, $r_h = 2b$, as a threshold to a broken state of the bond. This convention is based on our checks that the probability for recombination of bonds, stretched beyond r_h, is sufficiently small.

3 Simulation Results

3.1 Equilibrium Properties

We have checked typical properties of the strongly adsorbed brush molecules as the variation of the mean radius of gyration R_g^2 and the mean end-to-end distance between terminal points on the polymer backbone, R_e^2, for several lengths of the side chains, N - see Fig. 2a. One can easily verify from Fig. 2a, that the structure of the bottle-brush indicates a typical quasi-$2d$ behavior, as one would expect for the case of strong adsorption. One observes a scaling behavior $R_g^2 \propto L^{2\nu}$ where the
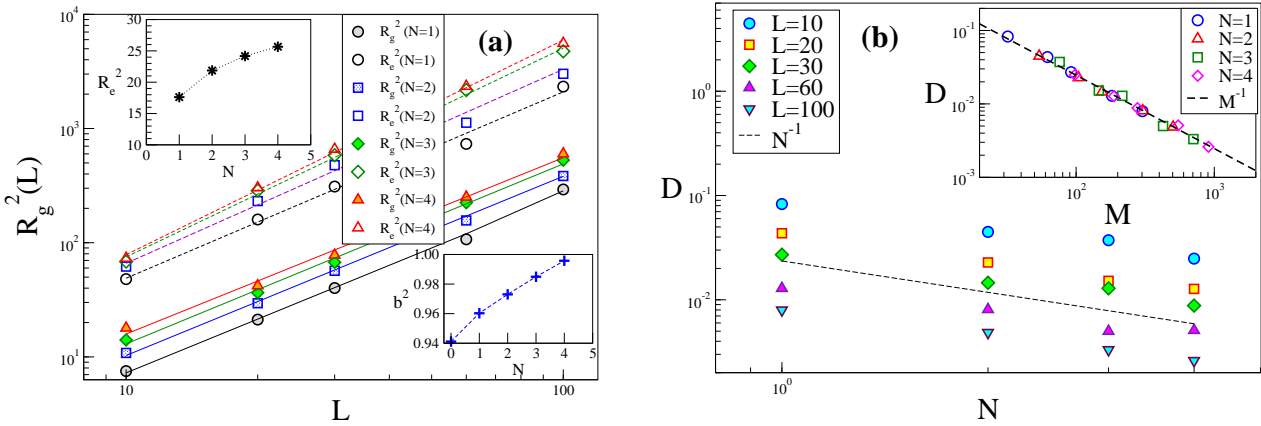

Figure 2: (a) Variation of the gyration radius R_g^2 and the end-to-end distance R_e^2 with the degree of polymerization L in a brush molecule for side chains of length N. Lines denote a scaling relationship $R_g^2 \propto R_e^2 \propto L^{2\nu}$. Insets show the increase of R_e^2 and the mean squared bond length b^2 with changing side chain length N for $L = 30$. (b) Diffusion coefficient D vs N for brush molecules of different length L. In the inset D is plotted against the total number of monomers in the bottle-brush macromolecule $M = L + 2N(L + 1)$. The dashed straight line indicates a $D \propto N^{-1}$ power law.

power-law Flory exponent attains a value $\nu = 0.76 \pm 0.01$ that is close to the exact one, $\nu_{2d} = 3/4$. From the insets in Fig. 2 one can see that the end-to-end distance , R_e^2, of the backbone steadily increases with growing length N of the side chains. The same applies for the mean bond length b^2 between segments along the backbone as function of N. Evidently, due to the high grafting density the side chains repel and stretch each other into an extended conformation. The steric repulsion between side chains is strongly enhanced when the macromolecule is adsorbed and attains a quasi-twodimensional conformation. As a result, both its contour and persistent lengths are increased.

3.2 Scission Probability Histogram

We examine the distribution of scission probability (the probability of bond rupture) along the polymer backbone for the case of a strong adsorption, $T = 0.10$, $\epsilon_s = 0.5$ in Fig. 3. One can readily verify from Fig. 3a that for a given contour length L the shape of the probability histogram changes qualitatively as the length of side chains N is increased beyond one, $N > 1$. While for $N = 1$
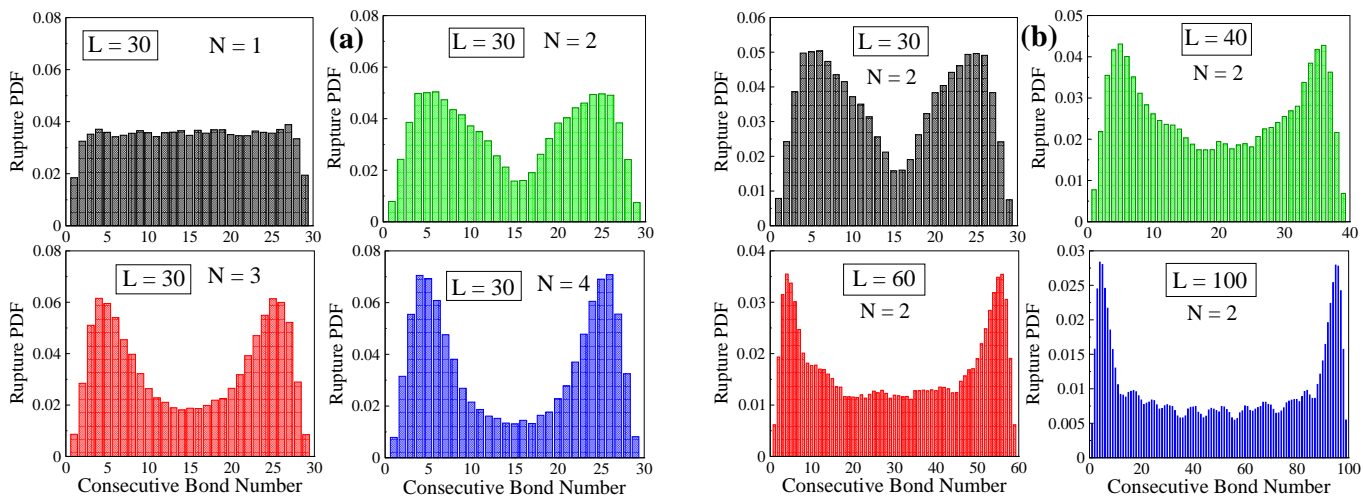

Figure 3: (a) Scission probability histogram for a polymer backbone with $L = 30$ and different length of the side chains N. (b) Variation of the scission probability histogram with contour length L for brush molecules with fixed side chain length $N = 2$.

the scission probability is uniformly distributed along the backbone (being significantly diminished only in the vicinity of both terminal bonds), for $N > 1$, in contrast, one observes a well expressed minimum in the probability in the middle of the chain in between the two pronounced maxima ("horns") close to the chain ends. This effect persists and is even enhanced as the contour length L gets larger - Fig. 3b. Occasionally, some additional maxima show up in longer molecules, $L > 30$, which are then found to disappear with improved statistics. We have tracked down these temporal maxima in the scission probabilities as corresponding to local bends and kinks in the contour which, owing to mutual squeezing or rarefaction, strongly change the side chains mobility and, presumably, the induced tension. Since conformations of adsorbed long molecules change rather slowly, a very large number of simulation runs is needed before such spurious maxima disappear.

Evidently, with growing length N of the side chains the minimum gets deeper and broader,

indicating that breakage happens most frequently in bonds which are very close to the terminal bonds of the backbone. Given the high density of grafting, one may interpret this effect as a consequence of the mutual immobilization and blocking of the side chains which are placed in the middle. In comparison, side chains that are closer to the ends of the polymer backbone still have sufficient freedom to move and, therefore, contribute locally to stronger tension in the vicinity of both ends of the backbone. Side chains of length $N = 1$, on the other hand, are too short to block one another. Therefore brush molecules with $N = 1$ behave similar to such with longer side chains but at sufficiently lower grafting density.

3.3   Dependence of $\langle \tau \rangle$ on L

In Fig. 4a we show the dependence of the mean time before any of the backbone bonds breaks, i.e., the MFBT $\langle \tau \rangle$ on the contour length L and on the total number of segments in the bottle-brush molecule $M = L + 2N(L + 1)$. Evidently, one observes a well expressed power law, $\langle \tau \rangle \propto L^{-\alpha}$ with exponent $\alpha \approx 0.17$. Since for large L one has $M \propto L$, the variation of $\langle \tau \rangle$ with M is the same. This
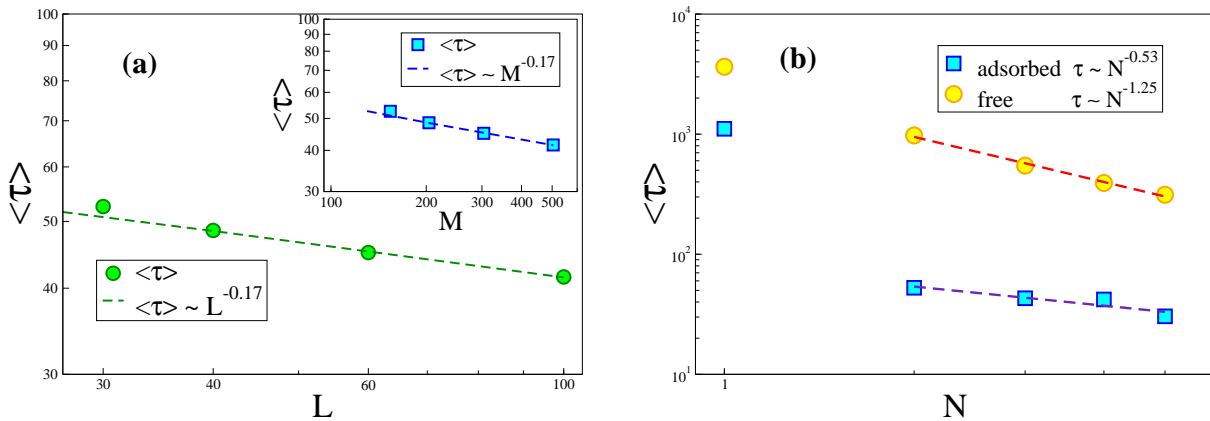

Figure 4: (a) Variation of the MFBT $\langle \tau \rangle$ with contour length L and with total number of monomers M of the brush molecule (inset) for length of the side chains $N = 2$. Here $k_B T = 0.10$. (b) Mean life time $\langle \tau \rangle$ vs N for a desorbed (free) and adsorbed brush molecule with $L = 30$.

finding is important because it indicates that $\langle \tau \rangle$ depends rather weakly on the total number of bonds that might break, in clear contrast to thermal degradation of polymers without side chains [23] where $\alpha = 1$. Indeed, when bonds break uncorrelated and entirely at random, the probability that *any* of the L bonds may undergo scission within a certain time interval should be proportional

to the total number of bonds, and therefore $\langle\tau\rangle \propto 1/L$. In cases of chain scission when a constant external force pulls at the ends of the polymer, however, one finds typically $\alpha < 1$ [24] whereby the value of α steadily decreases as the force strength grows. This suggests a gradual crossover from a predominantly individual to a more concerted mechanism of bond scission. In adsorbed bottle-brush molecules it is the side chains that induce tension in the polymer backbone and thus lead to rupture behavior similar to that with external force.

In Fig. 4b we compare the dependence of $\langle\tau\rangle$ on length N of the side chains, comparing non-adsorbed (free) and adsorbed brush molecules of length $L = 30$. As far as the side chains are rather short, one should not overestimate the observed power-law dependence, with $\langle\tau\rangle \propto N^{-1.25}$ for free, and $\langle\tau\rangle \propto N^{-0.53}$ for strongly adsorbed molecules. Generally, adsorption is found to diminish the mean rupture time by more than an order of magnitude alone, at least for $N > 1$. As mentioned before, the case $N = 1$ where neighboring side chains almost do not overlap is qualitatively different so, upon adsorption, the MFBT shortens by a factor of three only.

3.4   Fragment Size Distribution

In the present work we studied the fragmentation kinetics and the resulting molecular weight distribution, $P(n,t)$, of strongly adsorbed bottle-brush molecules for the shortest side chains $N = 1$, - see Fig. 5 - since, as shown above, they do not mutually overlap very strongly and produce a scission probability distribution for the bonds along the polymer backbone that matches the one, inferred from experiment [17]. If one assumes that the scission kinetics is described by a first-order reaction, then one may describe the decrease in the average contour length of the fragments with elapsed time [18, 19] as

$$\left(\frac{1}{L(t)} - \frac{1}{L_\infty}\right) = \left(\frac{1}{L_0} - \frac{1}{L_\infty}\right) e^{-kt}, \tag{5}$$

where L_0 is the initial contour length at $t = 0$ and L_∞ is the mean contour length of polymer chains at infinite time. The lower limit of the chain length of fractured molecules is ascribed to reduction of the backbone tension as molecular brushes with short backbones adopt a more relaxed conformation. In Fig. 6a we show the length distributions of the degradation products at different times after the onset of the scission process. The shapes of $P(n,t)$ are found to agree well with the experimentally observed ones [18] even though our species are about an order of magnitude
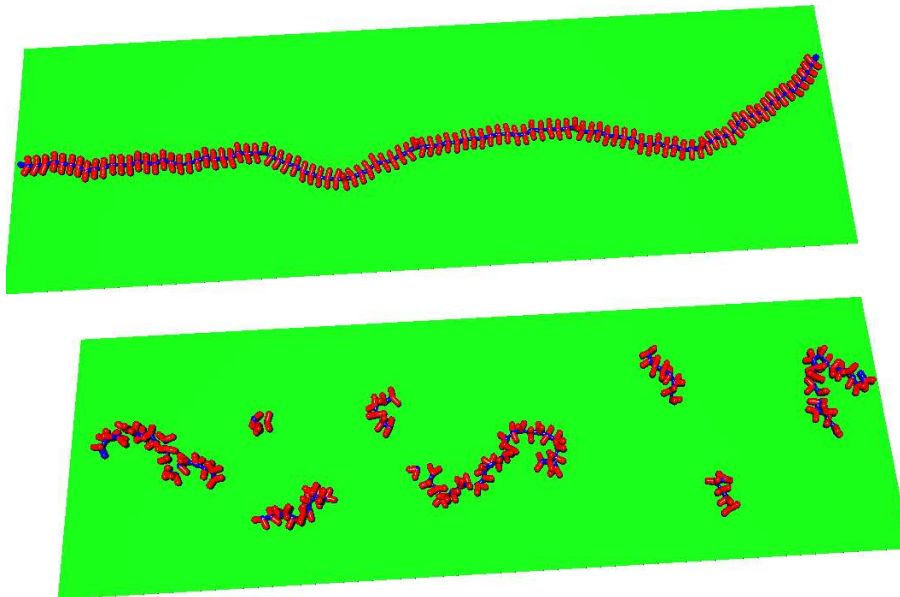
Figure 5: Snapshots of an adsorbed bottle-brush macromolecule (a "centipede") with backbone length $L = 100$ and side length $N = 1$ at $T = 0.12$ and $\epsilon_s = 0.50$ before (above) and after (below) the fragmentation process is completed at $t = 600$ $t.u.$

smaller than in the laboratory experiment, and the side chains - even more. In the beginning of the degradation, $t = 0.2 \div 0.4$, one can still observe a $\delta-$function-like peak at the initial length $L_0 = 100$ of the backbone. At later times $t \geq 0.4$, the distribution goes over into a rather flat one with a maximum around size $n \approx 10$. Eventually, one ends up with a rather sharply peaked $P(n, t = 29)$ at sizes $n \approx 1 \div 4$ which yields $L_\infty(t \gg 1) \approx 7.5$ at late times. Bonds in brush molecules of size $n = 7$ and shorter remain resistant to cleavage over very long periods of time. Following the theoretical consideration by Panyukov et al. [21], one would conclude that the maximum tension along the brush backbone, $f \approx \frac{k_B T}{b} L_\infty$ has fallen below the threshold necessary for rupture.

The variation of the mean fragment size $L(t)$ appears to be qualitatively well described by the theoretical expression, Eq. (5), apart from some small deviations at the crossover between initial fast fragmentation and a very slow subsequent decline of $L(t)$ - Fig. 6b. Our data suggest a value for the rate constant $k = 0.25$.

Thus the simulation data, presented in Fig. 6, appear to support the basic assumption that leads to Eq. (5), namely that every bond scission results in a new molecule. One may therefore conclude that recombination of bonds during the degradation process plays a negligible role under
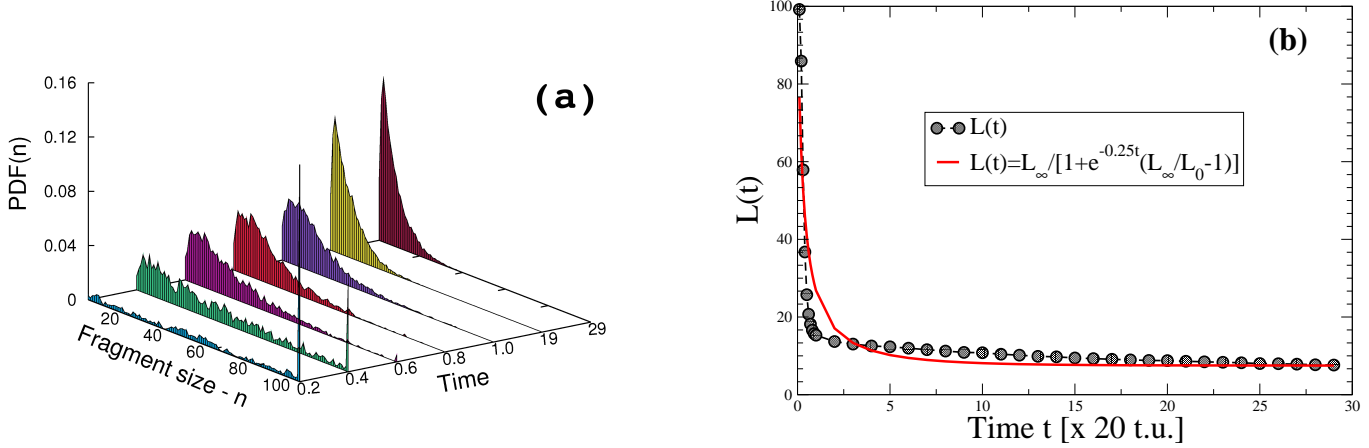
Figure 6: (a) Probability distribution of fragment sizes $P(n,t)$ at different times t (in units of 20 MD t.u.) after beginning of the fragmentation process for a brush molecule on a substrate with $L = 100$, $N = 1$. (b) Variation of the mean fragment length $L(t)$ after the onset of thermal degradation for a brush molecule with $L_0 = 100$ and $L_\infty = 7.5$. The solid line denotes the theoretical result, Eq. (7).

the current choice of parameters.

4   Concluding Remarks

. In this work we have used a MD simulation to model the process of thermal degradation in strongly adsorbed bottle-brush molecules. Our results confirm the strong effect of adsorption on chain scission, owing to an enormous increase in backbone tension, predicted theoretically [21]. This has been indeed observed in recent experiments [17, 18, 19]. Since the chemical nature of the bonding interactions remains unchanged, the observed adsorption-induced bond cleavage is of purely mechanical origin and is due to the conformational changes which a branched molecule undergoes when the energy gain by contact with the surface confines the molecule in a quasi-2d shape.

Among the main results of our investigation one should note

- static (R_g^2, R_e^2) and dynamics (diffusion coefficient D) properties of strongly adsorbed bottle-brush molecules on a substrate reveal a typical behavior of quasi-2d objects with scaling exponent $\nu = 3/4$.

- The mean life time of a bond $\langle\tau\rangle$ becomes more than an order of magnitude shorter upon

adsorption of a free bottle brush molecules on adhesive surface

- The mean life time $\langle \tau \rangle$ decreases weakly with growing contour length L of the backbone, $\langle \tau \rangle \propto L^{-0.17}$, and faster, $\langle \tau \rangle \propto N^{-0.53}$ with the length of the side chains, N.

- The probability distribution for rupture is sensitive to the grafting density of the side chains - the shape of the scission probability distribution resembles the experimentally established one only at lower grafting density when the side chains do not overlap strongly.

- The length distribution $P(n,t)$ and the average length of fragments, $L(t)$, during the degradation process are found to agree well with the respective ones, observed in experiments. Our data confirm the basic assumption for the scission kinetics as a first order chemical reaction.

Generally, one may therefore conclude that our model provides an adequate description of the behavior of bottle-brush molecules during fragmentation. Of course, many aspects of the adsorption-induced thermal degradation may and should be explored in much more detail than in the present study. We plan to report on such investigations in a future work.

5   Acknowledgments

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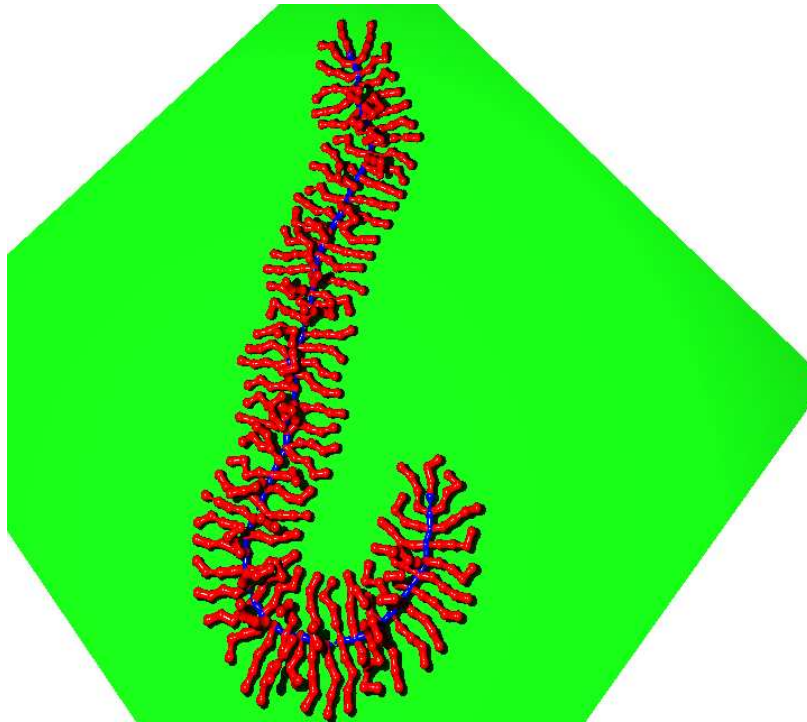
Figure 7: TOC graph: A bottle-brush molecule with $L = 60$ backbone monomers and 122 side chains of length $N = 4$. Here $k_B T = 1$ and the adsorption strength $\epsilon_s = 9.5$.