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

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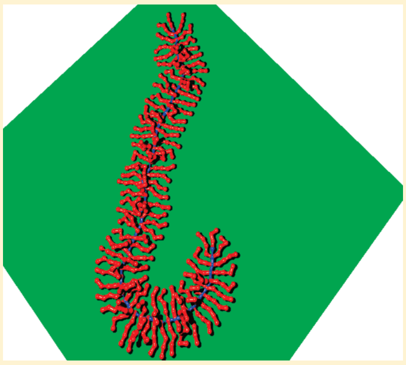

ABSTRACT: The scission kinetics of bottle-brush molecules in solution and on an adhesive substrate is modeled by means of molecular dynamics simulation with Langevin thermostat. Our macromolecules comprise a long flexible polymer backbone with L segments, consisting of breakable bonds, along with two 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 lifetime $\langle\tau\rangle$ decreases upon adsorption by more than an order of magnitude even for brush molecules with comparatively short side chains $N = 1-4$. 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 lifetime $\langle\tau\rangle$ 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 indicates the possibility that two different mechanisms may govern the fragmentation process.

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.[5−14] The main assumptions 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 (nonlinear) 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[17−19] that covalent bonds may spontaneously break upon adsorption of brushlike macromolecules onto a substrate. One studied brushes consisting of a poly(2-hydroxyethyl methacrylate) 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 lifetime.[20] Thus, one may observe amplification of bond tension from the piconewton to nanonewton 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 brushlike 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 $f_0 \approx k_B T/b$

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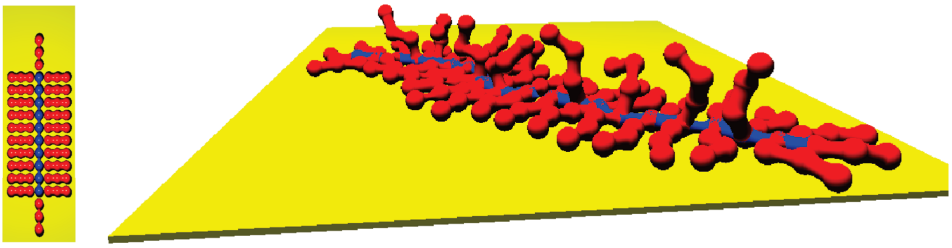

Figure 1. (left) Staring configuration of a bottle-brush molecule (a "centipede") with $L = 10$ (backbone) and $N = 3$ (side chain), so that the total number of segments $M = 76$. (right) A snapshot of a thermalized "centipede" with $L = 20$ backbone monomers (blue) and 42 side chains (red) of length $N = 4$. The total number of beads is $M = 188$. Here $k_BT = 1$ and the strength of adsorption $\varepsilon_s = 9.5$. Side chains which are too strongly squeezed by the neighbors when the backbone bends are seen occasionally to get off the substrate in order to minimize free energy.

with k_B being the Boltzmann constant and 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 macromolecules, 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 adsorbed 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

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

with a parameter $\alpha \equiv 1$. The dissociation energy of such bonds is D, measured in units of k_BT, 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)

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

with $\Theta(x) = 0$ or 1 for $x < 0$ or $x \geq 0$, and $\varepsilon = 1$. The nonbonded 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:

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

The random force which represents the incessant collisions of the monomers with the solvent molecules satisfy the fluctuation–dissipation theorem $\langle R^i_\gamma(t)R^j_\delta(t')\rangle = 2\zeta k_BT\delta_{ij}\delta_{\gamma\delta}\delta(t - t')$. 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 $(m/\sigma^2D)^{1/2}$ 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.

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 there are three side chains anchored. 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 $N = 1-5$ in our simulations (Figure 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 nonlinear elastic" (FENE) potential

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

In eq 4 $k = 30$ and $r_0 = 1.5$, 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, $U_{LJ}(z) = 4\varepsilon_s[(\sigma/z)^{12} - (\sigma/z)^6]$. In our simulations we consider as a rule the case of strong adsorption, $\varepsilon_s/k_BT = 5.0-10.0$.

The initially created configurations (Figure 1, left panel) are equilibrated by MD for a period of time so that the mean-square displacement of the polymer center-of-mass moves a distance several (3–5) times larger than the polymer size (i.e., larger than

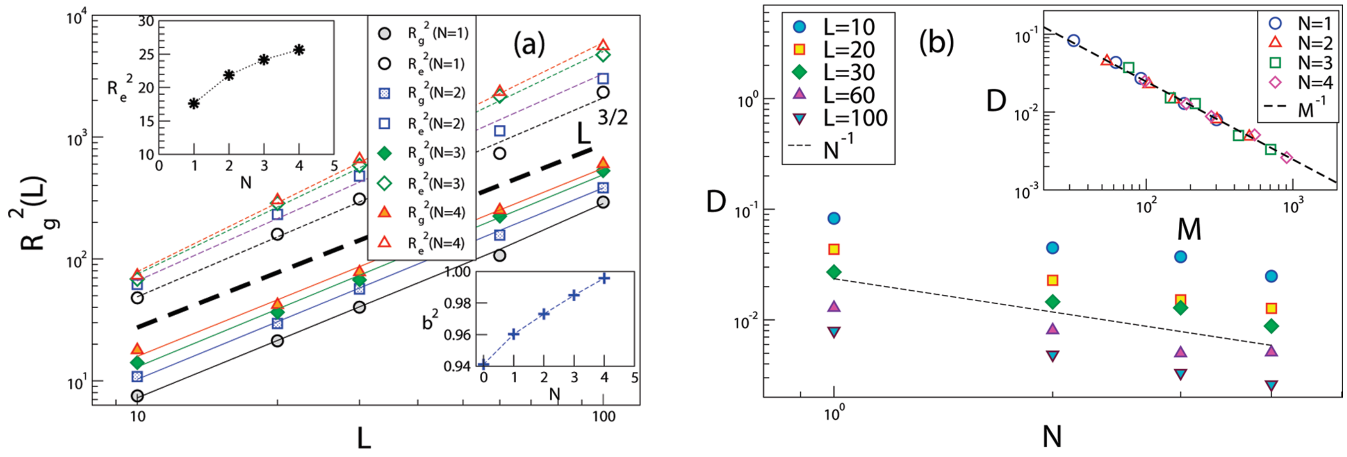

Figure 2. (a) Variation of the gyration radius R_g^2 and the end-to-end distance R_e^2 with the degree of polymerization L in a brush molecule for side chains of length N. Lines denote a scaling relationship $R_g^2 \propto R_e^2 \propto L^{2\nu}$. The (asymptotically) exact scaling, $R_g^2 \propto L^{3/2}$, is indicated by a bold dashed line for comparison. Insets show the increase of R_e^2 and the mean-squared bond length b^2 with changing side chain length N for $L = 30$. Here and in (b), $T = 1.0$ and $\varepsilon_s = 9.5$. (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.

the radius of gyration, R_g). During this period no scission of backbone bonds may take place. We then start the simulation with a well-equilibrated conformation of the chain and allow thermal scission of the bonds. We measure the mean lifetime 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, $L(t)$. One should point out that we perform our computer experiment in a somewhat more idealized way than in a laboratory. It is possible that in the latter case the chains begin to break even during the process of adsorption so that the lower bound of lifetime τ becomes difficult to determine under well-defined conditions. Therefore, in our computer experiment we work at sufficiently low temperature T so that the first scissions occur after reasonably large waiting time.

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 some typical properties of the strongly adsorbed brush molecules as the scaling 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, with backbone length L for several lengths of the side chains, N (see Figure 2a). One can easily verify from Figure 2a that the structure of the bottle-brush macromolecules 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 power-law Flory exponent attains a value $\nu = 0.77 \pm 0.02$ that is close to the asymptotically exact one, $\nu_{2d} = 3/4$.[23] However, the observed values of ν appear systematically somewhat higher than $\nu_{2d} = 3/4$ (the latter is indicated in Figure 2a by a thick dashed line). A closer inspection of the displayed scaling behavior reveals even a small yet systematic increase in the R_e^2 vs L slope as the length N of the side chains grows.

On the other hand, from the insets in Figure 2a one can see that the end-to-end distance of the backbone, R_e^2, itself 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 a function of N. Evidently, due to the high grafting density, the side chains progressively repel and stretch each other into an extended conformation as they get longer. Naturally, the steric repulsion between side chains is strongly enhanced when the macromolecule is adsorbed and attains a quasi-two-dimensional conformation.[21] As a result, both its contour and persistent lengths are increased; that is, with growing N the polymer becomes stiffer. Since the studied lengths L are not very large, the macromolecules do not accommodate sufficiently many persistent lengths and manifest a scaling behavior in between that of entirely flexible polymer chains with $\nu = 3/4$ and rigid rods with $\nu = 1.0$.

Similar to the static properties, discussed above, the diffusion coefficient $D = k_BT/\zeta$ of adsorbed bottle-brush molecules (Figure 2b) reveals a typical Rouse-like behavior, representative for the so-called "free draining limit" when the friction ζ of a M-bead polymer coil in the solvent is simply M times larger that the friction of an individual bead ζ_0, that is, $\zeta = M\zeta_0$. This is indeed manifested in the inset in Figure 2b. Less trivial is the dependence of D on the length of side chains, N. When the side chains get longer, $L \ll M$, the total number of segments in the "centipede" M becomes nearly proportional to N, and a $D \propto N^{-1}$ dependence is to be expected, as one can verify from Figure 2b.

As far as the present computer experiment employs Langevin dynamics where the solvent is only implicitly taken into account,

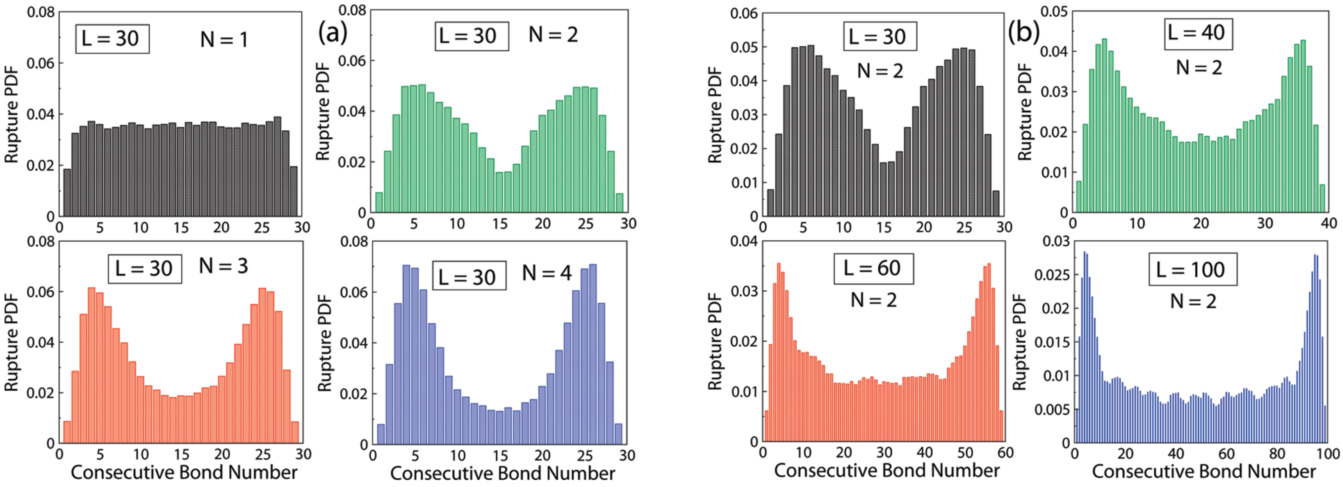

Figure 3. (a) Scission probability histogram for a polymer backbone with $L = 30$ and different length of the side chains N. (b) Variation of the scission probability histogram with contour length L for brush molecules with fixed side chain length $N = 2$.

one might wonder if our results would change in a system with explicit solvent being present. It is known, however, that then the long-range effect of a planar wall on the mobility of a particle decays as $1/h$, where h is the distance from the wall.[24] Therefore, at least for strongly adsorbed bottle-brush molecules we believe that hydrodynamic interactions will have virtually no effect on polymer dynamics.

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, $T = 0.10$, $\varepsilon_s = 0.5$, in Figure 3. One can readily verify from Figure 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 $N = 1$ 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 (Figure 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 are 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.

It is interesting to note that for polymers with *no* side chains, which undergo a thermal degradation process in the bulk, the scission rate is minimal for the terminal bonds[25] even though the mobility of the end monomers exceeds that of the middle ones.

3.3. Dependence of $\langle \tau \rangle$ on L. In Figure 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 $M = L + 2N(L + 1)$. $\langle \tau \rangle$ was obtained as a first moment of the probability distribution of lifetimes, $W(\tau)$ (not shown here), which looks very much like a Gaussian distribution with a slight asymmetry (a somewhat longer tail at the large times) . Evidently, in Figure 4a one observes a well-expressed power law, $\langle \tau \rangle \propto L^{-\beta}$ with exponent $\beta \approx 0.17$. Since for large L one has $M \propto L$, the variation of $\langle \tau \rangle$ with the total number of segments M is the same.

This 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[25] where $\beta = 1$. 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 $\beta < 1$,[26,27] whereby the value of β 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 Figure 4b, we compare the dependence of $\langle \tau \rangle$ on length N of the side chains, comparing nonadsorbed (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 desorbed, 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

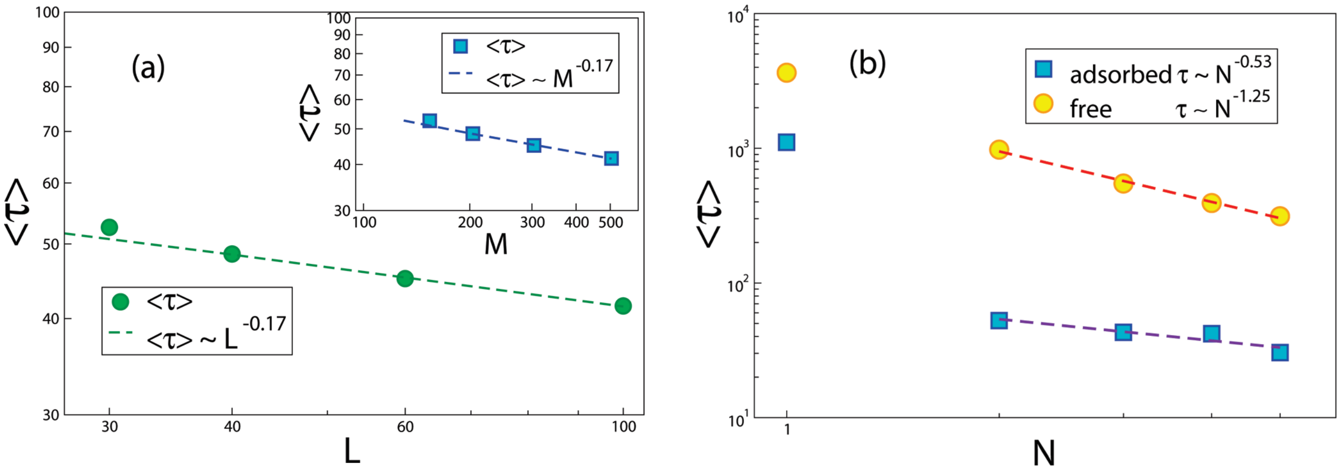

Figure 4. (a) Variation of the MFBT $\langle\tau\rangle$ with contour length L and with total number of monomers M of the brush molecule (inset) for length of the side chains $N = 2$. Here $k_BT = 0.10$ and $\varepsilon_s = 0.50$. (b) Mean lifetime $\langle\tau\rangle$ vs N for a desorbed (free) and adsorbed brush molecule with $L = 30$.

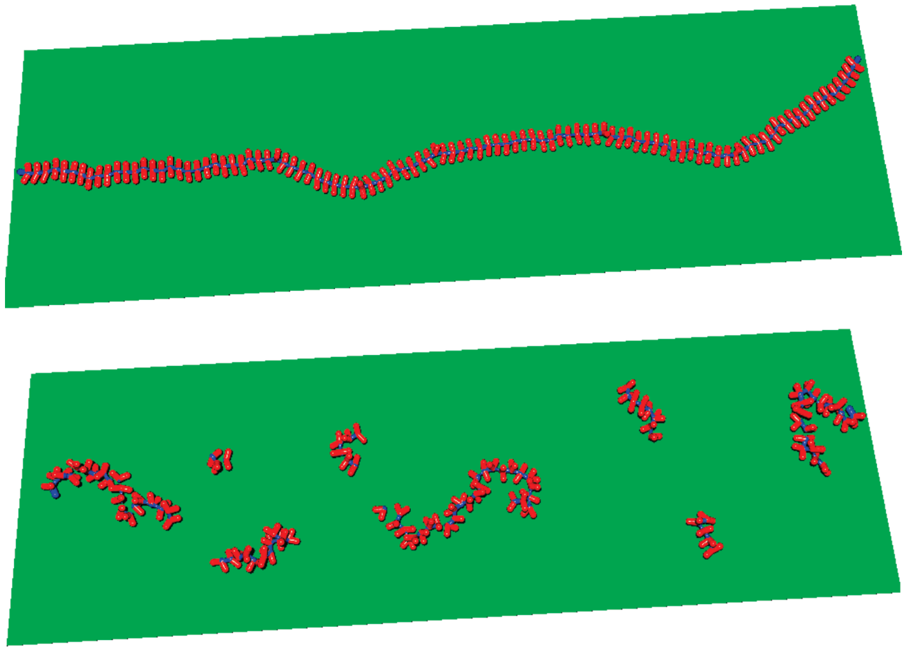

Figure 5. Snapshots of an adsorbed bottle-brush macromolecule (a "centipede") with backbone length $L = 100$ and side length $N = 1$ at $T = 0.12$ and $\varepsilon_s = 0.50$ before (above) and after (below) the fragmentation process is nearly completed at $t = 600$ t.u.

case $N = 1$ where neighboring side chains almost do not overlap is qualitatively different so, upon adsorption, the MFBT shortens by a factor of 3 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 $N = 1$, 2 (see Figure 5) since, as shown above, for $N = 1$ 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] In contrast, the case $N = 2$ leads to bond rate histogram which qualitatively resembles those with $N > 2$ and can, therefore, be viewed as representative for the longer side chains. As usual, $P(n,t)$ denotes the probability to find a fragment of size n at time t after the onset of the degradation process.

One can easily derive an expression for the time evolution of the mean backbone length, $L(t) = \int nP(n,t)\, dn$, provided some basic assumption is made in regard of the bond scission kinetics.

(i) If one assumes that the scission kinetics is described by a *first-order* reaction, then for irreversibly breaking bonds one may describe the rate of scission as

$$\frac{dm(t)}{dt} = -k(m(t) - m_\infty) \qquad (5)$$

where the number of intact bonds in the system at time t is $m(t)$, and k denotes the relevant kinetic constant. In eq 5, m_∞ is the number of intact bonds at late times, $t \to \infty$. Equation 5 is then easily solved to

$$m(t) = (m_0 - m_\infty)e^{-kt} + m_\infty \qquad (6)$$

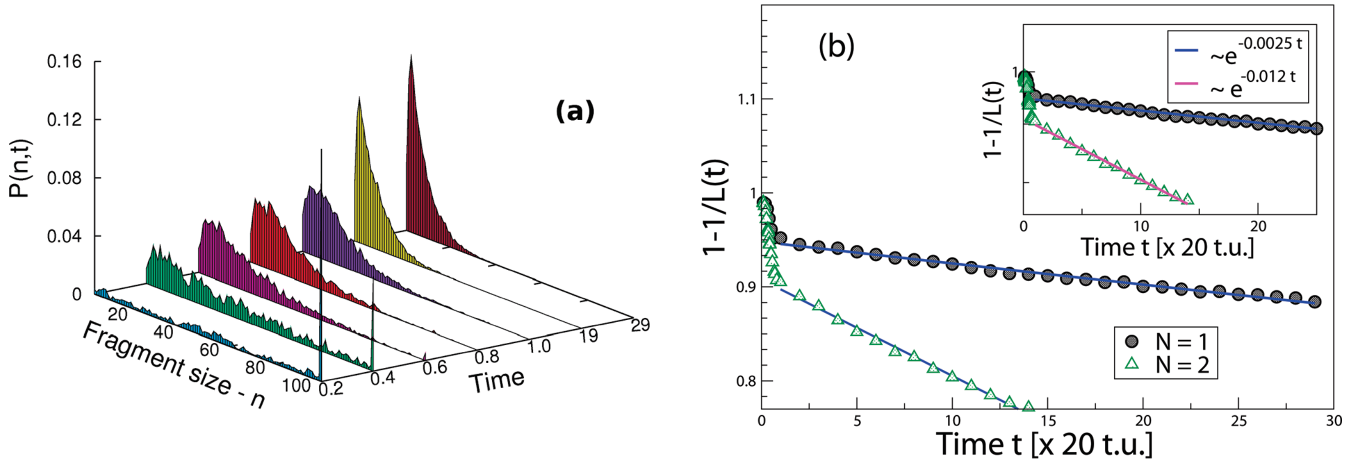

Figure 6. (a) Probability distribution of fragment sizes $P(n,t)$ at different times t (in units of 20 MD t.u.) after beginning of the fragmentation process for a brush molecule on a substrate with $L = 100$, $N = 1$ at $T = 0.12$, $\varepsilon_s = 0.5$. (b) Variation of the mean fragment length, taken as $1 - L(t)^{-1}$, for a brush molecule with side chains $N = 1$ (circles) and $N = 2$ (triangles). In the inset the same is shown in semilogarithmic coordinates with the respective kinetic constants indicated in the legend. Solid lines denote the theoretical results, eq 8, and eq 10 with $L_\infty = 1$.

where $m_0 = m(t{=}0)$. If the total number of bonds in the system is M, then the average contour length $L(t)$ of all fragments at time t will be

$$L(t) = \frac{M}{M - m(t)} \tag{7}$$

since the number of fragments in the system is given by the number of broken bonds. For the mean contour length $L(t)$ one then gets an expression, derived in 1939 by Wolfrom et al.[28]

$$\frac{1}{L(t)} - \frac{1}{L_\infty} = \left(\frac{1}{L_0} - \frac{1}{L_\infty}\right) \mathrm{e}^{-kt} \tag{8}$$

where $L_0 = M/(M - m_0)$ is the initial contour length at $t = 0$ and $L_\infty = M/(M - m_\infty)$ is the mean contour length of backbone fragments at infinite time $t \to \infty$. In fact, L_∞ denotes the minimal size of a cluster that does not disintegrate any further. This lower limit of the chain length of fractured molecules can be ascribed to reduction or even vanishing of the backbone tension.

(ii) Alternatively, one may assume, that the scission rate is constant and independent of the number of intact bonds at time t, that is, $\mathrm{d}m(t)/\mathrm{d}t = -k$, which corresponds to a *zero-order* chemical reaction. Instead of eq 7, one obtains then

$$m(t) = m_0 - kt, \quad 0 \le t \le \frac{m_0}{k} \tag{9}$$

where the process exists in time as long as all bonds get broken. For the mean contour length $L(t)$ it follows

$$1 - \frac{1}{L(t)} = \left(1 - \frac{1}{L_0}\right) - k't \tag{10}$$

with $k' = k/M$. This second scenario could correspond to a strong degree of collectivity in bond scission events, as discussed by us in ref 27 for the case of polymer chain scission at constant external tensile force. It also appears more consistent with the observed rather weak dependence, $\langle\tau\rangle \propto L^{-0.17}$, shown in Figure 4a, as opposed to the case of an independent bond scission scenario where one should observe $\langle\tau\rangle \propto L^{-1}$.[27]

In Figure 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 smaller than in the laboratory experiment and the side chains—even more. In the beginning of the degradation, $t = 0.2-0.4$, one can still observe a δ-function-like peak at the initial length $L_0 = 100$ of the backbone. Later, for $t \ge 0.4$, the distribution goes over into a rather flat one with a maximum around size $n \approx 20$. Eventually, one ends up with a rather sharply peaked $P(n,t{=}29)$ which yields $L(t{=}600) \approx 7.5$. At late times, $t > 600$, the process goes steadily on until finally the limit of $L_\infty = 1$ is reached.

In Figure 6b, we plot the evolution of the mean fragment length $L(t)$ by using the quantity $1 - L(t)^{-1}$ which is more appropriate in order to expose the true kinetics of the fragmentation process. It is immediately seen from Figure 6b that the bottle-brush fragmentation comprises a two-stage process whereby an initial very short and steep decay is followed by a much longer, albeit slower, one.

In view of Figure 6b, one might assume that the maximum tension along the brush backbone, $f \approx f_0 N$,[21] depends implicitly on L, too. The tension is quickly relaxed below a threshold $f_{\mathrm{th}}(L, N)$ when the backbone fragments get short enough so that below a critical length L_{th} the side chains experience much weaker steric repulsion. In our computer experiments with an initial length $L_0 = 100$ this happens at $L_{\mathrm{th}}/L_0 \approx 20\%$ when $N = 1$ and at $L_{\mathrm{th}}/L_0 \approx 10\%$ when $N = 2$. As expected, L_{th} steadily decreases when the length of the side chains grows, as our data on $N = 3$, 4 (not shown) suggest. For $L \le L_{\mathrm{th}}$, the fragmentation proceeds with a significantly smaller kinetic constant. Such an effect has not been reported in the laboratory experiments,[18,17] but it cannot be ruled out that the observations there refer to the lengthy secondary fragmentation whereas the initial quick drop of the mean length $L(t)$ lasts too short so as to be detected.

Somewhat surprisingly, the initial and the secondary fragmentation processes can be represented as nearly perfect straight lines in both normal and semilog coordinates! It appears, therefore, that the observed fragmentation kinetics cannot be unambiguously qualified as a first- or zero-order chemical reaction. In view of the observed rather weak dependence of the mean lifetime on polymer length, $\langle\tau\rangle \propto L^{-0.17}$ (see Figure 4a), the second scenario, eq 10, appears even the more probable. As expected, the rate of fragmentation is, of course, much higher for the longer side chains with $N = 2$. Moreover, one may conclude that recombination of bonds plays a negligible role during the degradation process.

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.[17−19] 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 the following:

- 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 lifetime 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 lifetime $\langle\tau\rangle$ 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. However, the studied lengths N of the side chains are too short for a definite scaling law to be established.
- The probability distribution for rupture is sensitive to the degree of steric repulsion of the side chains—the shape of the scission probability distribution resembles the experimentally established one only for weaker repulsion 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 albeit the accumulated tension in the backbone is released in two stages. A very short interval of fast breakage down is to about 20% of the initial mean length of the molecule is followed by a considerably slower process which lasts until the chain breaks down to fragments of the size of individual repeat units.
- The measured variation of the mean fragment size with time appears compatible with both first- and zero-order reaction kinetics, indicating the role of collective effects in the process of bond scission.

Generally, the present study may be regarded as a first attempt to get a deeper insight in the fascinating behavior of adsorbed 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.

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