

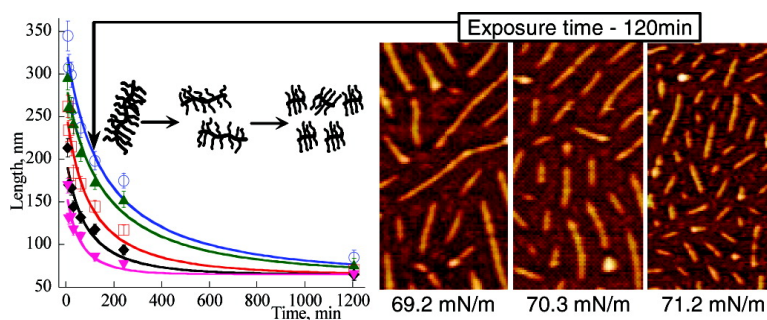
Communication

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“Fatal Adsorption” of Brushlike Macromolecules: High Sensitivity of C–C Bond Cleavage Rates to Substrate Surface Energy

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Recently, we have initiated studies aimed at unraveling the physics of unprecedented mechanochemical degradation of brushlike macromolecules (Figure 1a), dubbed “fatal adsorption”.¹ The adsorption and subsequent spreading of the polymer molecules is driven by their propensity to maximize the number of contacts between the monomeric units and the substrate and thus to lower the overall free energy. As the densely grafted side chains adsorb, they experience steric repulsion 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.² Eventually this adsorption-induced tension may overcome the covalent bond strength and cause molecular fracture via C–C bond scission. We seek to determine the physicochemical properties of polymer and substrate that allow for conformational deformation and spontaneous breakage of the covalent backbone. In this communication, we report the kinetics of backbone scission as a function of substrate surface energy. We show that a few percent variations of the surface energy lead to orders of magnitude changes in the scission rate. The results have important implications for surface chemistry in general, and for specific applications such as sensors and microfluidics, where control of surface-induced changes in the primary molecular structure is vital.

In this work, we studied brushes consisting of a low polydispersity poly(2-hydroxyethyl methacrylate) backbone and poly(*n*-butyl acrylate) (PBA) side chains with number average degrees of polymerization of $N_n = 2150 \pm 100$ and $n = 140 \pm 5$, respectively. The polymers were prepared by Atom Transfer Radical Polymerization.^{3,4} Brush molecules were adsorbed from a dilute solution in chloroform on the surface of water/2-propanol mixtures in a Langmuir–Blodgett (LB) trough. Mixing water and 2-propanol allowed accurate control of the surface energy in the range of 69–71 mN/m (Table 1). 2-Propanol was chosen as a cosolvent because its vapor pressure is close to that of water, which minimizes changes of surface energy due to evaporation. Note that swelling of the brush side chains in the liquid subphase may cause additional variations of tension along the backbone. However, the swelling effect due to addition of 2-propanol is weaker than the surface interaction effect and it is of opposite sign. As shown below, the strength of adsorption decreases with adding 2-propanol and results in a decrease of tension along the backbone, while swelling-caused extension of the side chains should increase the tension. After spending different time intervals on the water/2-propanol substrates, polymer monolayers were transferred onto a mica surface (using the standard LB techniques) for AFM studies.⁵ Details of the AFM experiments and image analysis are described in our previous paper.¹

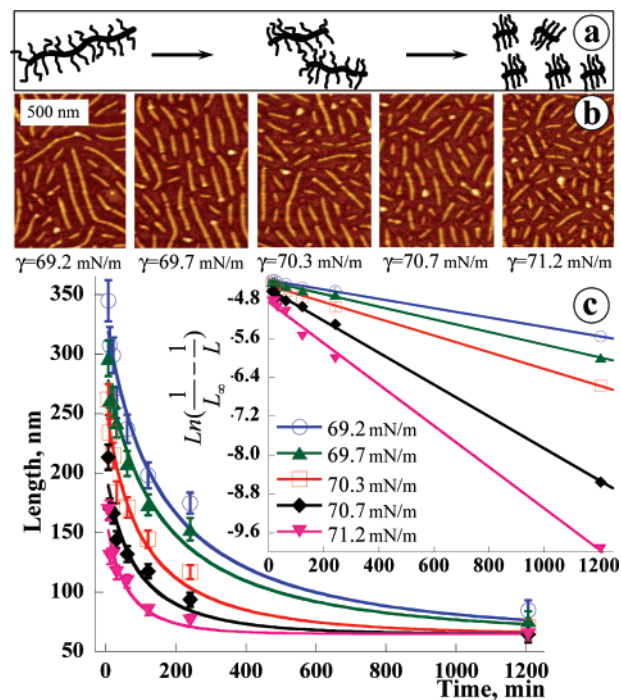


Figure 1. a) Schematic of the adsorption-induced molecular degradation process. b) AFM height images of brush polymers taken up on mica surfaces after spending 62 min on aqueous substrates with different surface tensions, γ . The white threads in the images correspond to the backbones of polymer brushes. The height contrast is enhanced by desorbed side chains segregated around the backbone. The area between the backbones is covered with adsorbed side chains. c) Kinetics of the decrease of the average polymer chain length (L) on substrates with different γ . Solid curves calculated using eq 1. Inset: Plot of $\ln(1/L_\infty - 1/L)$ vs time for different γ values. The slopes of the lines give the rate constants for the scission reaction.

Table 1. Experimental Parameters for Kinetic Measurements

% 2-propanol	γ , ^a mN/m	$k \cdot 10^5$, s ⁻¹	S , ^b mN/m	force, ^c nN	force, ^d nN
0.30	69.2	2.3 ± 0.4	21.0	2.73	3.23
0.25	69.7	2.7 ± 0.4	20.8	2.71	3.24
0.20	70.3	4.7 ± 0.9	21.5	2.79	3.27
0.15	70.7	7.4 ± 1.9	21.1	2.75	3.29
0.10	71.2	13.7 ± 3.6	21.8	2.84	3.32

^a Surface tension (Supporting Information). ^b Spreading coefficient (Supporting Information). ^c Estimated as $f = S \cdot d$, where $d = 130$ nm is the brush width. ^d DFT calculations from ref 2.

The molecular degradation process was monitored by measuring the average chain lengths taken directly from AFM images at different exposure times. Figure 1b shows representative height images of brush-type polymers, each of which was exposed to

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aqueous substrates with different surface energies for a time interval of 62 min. Clearly, the molecules are noticeably shorter on substrates with a higher surface energy. Figure 1c shows complete kinetic traces for different values of the surface energy. After long time intervals a limiting value of the average chain length ($L_\infty = 65 \pm 10$ nm) is reached, which is approximately the same for each value of the surface energy. The lower limit of the chain length of the fractured molecules is ascribed to reduction of the backbone tension as molecular brushes with short backbones adopt a more relaxed, starlike conformation.

$$L = \frac{1}{\frac{1}{L_\infty} + \left(\frac{1}{L_0} - \frac{1}{L_\infty}\right)e^{-kt}} \quad (1)$$

We assume that the reaction of unimolecular decomposition follows first-order kinetics. Equation 1 presents the time dependence of backbone length, where L_0 and L_∞ are the initial and final chain lengths, respectively, and k is a first-order rate constant. The equation is a modified version of the previously derived expression¹ including an exponential factor in the denominator which ensures accurate description of the degradation process at both long and short contact times.

Figure 1c depicts kinetic curves from eq 1 with $L_\infty = 65$ nm, and two fitting parameters, L_0 and k . The curves are linear when plotted on a logarithmic scale ($\ln(1/L_\infty - 1/L)$ versus time (see inset). This suggests monoexponential behavior of the cleavage process. Some nonlinearity was observed at the very short exposure times (<5 min, not shown here). The behavior at the initial stages of the adsorption process is ascribed to ill-defined tension variations within partially adsorbed molecules in the presence of the evaporating solvent. Here, we only discuss the later stages of molecular degradation that are fitted with a single exponent. Table 1 presents the k values obtained from these measurements. Here, the most striking observation is that the rate constants increase by almost an order of magnitude with a very small increment in surface tension of about 3%.

To analyze the kinetic data, it is instructive to compare the obtained k values to the data available in literature. Grandbois et al.⁷ stretched polysaccharide molecules to measure the rupture force for a Si–C bond. This work prompted Beyer et al.² to carry out DFT calculations of rupture forces as a function of time for different bond types, including the C–C bond. Values of the rupture forces corresponding to experimental k values obtained in the present work are depicted in Table 1, column 6. The rupture forces in our experiments were estimated as $f \approx S \cdot d$,¹ where S is the spreading coefficient and $d = 130$ nm is the brush width.⁶ They range from 2.47 to 2.57 nN, which exceeds the typical range 10–100 pN used for stretching of polymer chains⁸ and lie near the lower limit of the rupture forces measured in flow-induced scission of C–C bonds in solution.⁹ The rupture forces determined in our experiments are lower than the corresponding range obtained from the DFT calculations.² However, as noted in ref 2, the calculated rupture forces might be overestimated by about 30% due to unknown effects of the surrounding environment. Regardless of the difference in the absolute values, it is important to emphasize that both experiment and DFT calculations reveal a strong increase of the bond-scission rate upon the percentage increment of the applied force.

Length distributions of the degradation products at different reaction times are summarized in Figure 2. An insert depicts the change in the polydispersity index (PDI) with time, measured for all substrates used. As shown previously,¹ the distribution initially broadens with time due to random chain scission. At later stages, the PDI decreases and approaches a limiting value $\text{PDI}_\infty > 1$ due

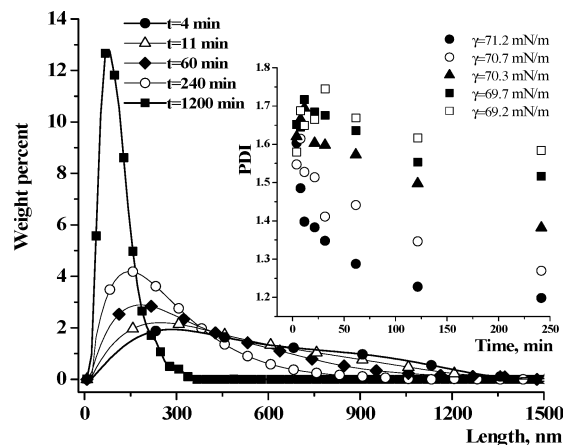


Figure 2. Experimental length distributions of the degradation products on the substrate with $\gamma = 69.2$ mN/m for different time intervals of the scission process. Inset: Variation of the polydispersity index $\text{PDI} = L_w/L_n$ with time for different γ values.

to the length distribution of the fractured macromolecules confined between L_∞ and 2^*L_∞ . The limiting PDI value depends on the bond-fracture probability distribution along the main chain of the brush macromolecules.

To summarize, our experiments show that the rate constant for adsorption-induced bond scission is extremely sensitive to the surface tension of the underlying substrate. Through manipulation of either surface tension or side-chain length, one can exert very precise control over the degradation kinetics in these polymers. For example, changing the side-chain length from 10 to 200 units on a water substrate alters the lifetime of the backbone C–C bonds from years to microseconds.

In this paper, we have considered only mechanically activated bond cleavage. One may argue that ester functionalities in PBA side chains are also susceptible to stress-induced hydrolysis. However, the adsorption-induced tension in the side chains is at least 1 order of magnitude lower than the tension in the main chain. Therefore, a hydrolysis mechanism is less likely. Ongoing experiments are focused on understanding the mechanism of adsorption-induced degradation of brushlike macromolecules and exploring the possibility of steering the course of chemical reactions¹⁰ offered by the architecture-controlled directionality of the tensile forces.

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Supporting Information Available: Determination of S for water/2-propanol mixtures and the dependence of γ on % of 2-propanol. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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