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Stress Relaxation in Telechelic Gels. 1. Sticker Extraction

F. Clément,[†] A. Johner,[†] J.-F. Joanny,*[,†] and A. N. Semenov[‡]

Institut Charles Sadron (UPR CNRS 022), L.E.A MPI Mainz/ICS Strasbourg, 67083 Strasbourg Cedex, France; and Department of Applied Mathematics, University of Leeds, Leeds, U.K.

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ABSTRACT: We discuss the nonlinear rheology of telechelic gels formed by triblock copolymers with short hydrophobic end blocks (the stickers). In this first paper, we merely study the variation of the extraction time of a sticker from a hydrophobic aggregate with the chain tension. Using a model potential that binds the sticker/chain junction point to the aggregate/water interface, we explicitly show that the extraction time only depends on the chain tension at the junction point. The results are extended to more realistic potentials by heuristic arguments. At this level of description various effects (curvature of the aggregate, sticker flexibility, impenetrable aggregate constraint) can also be accounted for.

1. Introduction

Considerable attention has been paid recently to hydrophobically modified polymers which have unique properties due to their ability to self-assemble and form transient networks where hydrophobic domains act as junction points.[1,2] The rheological response of those physical gels is very rich:[3] the viscosity increases by several orders of magnitude when the network forms; when a large deformation is imposed, the stress relaxes with time as the network structure adapts and these systems are shear thinning at high enough concentrations. There are two broad classes of hydrophobically modified polymers of special interest: end modified or telechelic polymers[4,5] and randomly modified polymers.[6,7] The structure and linear rheology of both types of polymers have been investigated theoretically by several authors.[8−11]

Soluble polymers with insoluble end blocks form flower micelles at low concentrations where the two end groups of each chain (the stickers) belong to the same hydrophobic aggregate. At higher concentrations flower micelles exchange stickers and bridges form between different micelles; a connected network is then obtained as sketched in Figure 1. The thermodynamics and the linear rheology of these networks have been described recently by Semenov et al.[8] at a scaling level. Flower micelles are described as star polymers[12] with soluble arms organized around the hydrophobic domain. As almost all hydrophobes are part of aggregates anyhow, the fraction of bridges as compared to loops is ruled by small entropic contributions to the free energy: it is small and increases with the polymer concentration. This description is based on binary interactions between flower micelles and is expected to be valid at moderate densities where bridging interactions are restricted to nearest neighbor micelles. At higher densities, each micelle is bridged to several other micelles further away. It has been show recently that main chain rigidity may strongly influence this structure,[13] in the remainder we only discuss flexible main chains.

The motion of a micelle in the network requires the destruction of the bridges with all of its neighbors. A "debridged" micelle can either move at the expense of compressing the surrounding micelles or creep at the expense of its own elastic deformation at almost conserved volume. At the flower-micelles overlap concentration c^*, the shear and compression moduli are comparable; the osmotic modulus is of the order of the osmotic pressure in the outermost corona of blobs. With increasing concentration the shear modulus becomes lower than the compression modulus. Micellar motion is easier at higher concentration where micelle creeping is the dominant mechanism. Three activation energies come into play for the micellar motion or the stress relaxation: the sticking energy of a hydrophobe (the energy barrier to extract one given hydrophobic group from the aggregate), the debridging energy (of the order of the thermal energy k_BT per bridge), the elastic penalty for the motion of a debridged micelle. The linear shear viscosity is obtained as the product of the shear modulus and the characteristic stress relaxation time; the stress relaxation time is of the order of the time needed by a micelle to move over its own size. The shear viscosity is predicted to jump by several orders of magnitude at the flower overlap concentration c^*; it further increases up to $\sim 2c^*$ and then decreases at higher concentrations (for not too high sticking energies only). The high concentration decrease, that would also be predicted for standard star polymers (nonbridging), has to our knowledge not yet been observed experimentally.

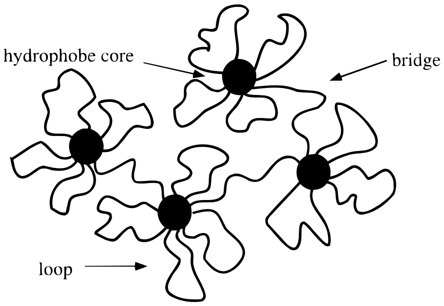

Figure 1. Telechelic gel comprising bridged micelles.

The detailed understanding of the hydrophobic sticker extraction from an aggregate appears therefore of special interest. In a planar geometry, for a flat polymer brush, it has been shown recently that due to chain stretching close to the interface, thermal sticker desorption is a local process essentially independent of the overall chain properties.[14] Similarly hydrophobe extraction from a hydrophobic domain should be a local

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[†] L.E.A MPI Mainz/ICS Strasbourg.

[‡] University of Leeds.

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process. The physical reason is that once the motion of the hydrophobe relaxes typically k_BT of the chain elastic energy, the outward motion is driven by chain tension and the extraction becomes irreversible. This local motion does not require any motion of the chain central monomer but only the motion of a small chain segment. The relevant friction is that of this short segment. The argument has been presented for a flat brush, pointlike sticking groups and thermally activated extraction with no applied external pulling force. In this paper, we study various models for the hydrophobe extraction, in particular with strong external pulling forces in order to describe the relaxation of the transient network at large deformations.

The paper is organized as follows. We first extend our previous analysis to the desorption of pointlike stickers promoted by a pulling force. We then discuss finite size stickers for which the sticker friction can compete with that of the (short) internal chain modes. Two types of hydrophobes are considered: rodlike stickers modeling short rigid hydrophobes and liquid deformable stickers (collapsed polymer blocks) modeling longer hydrophobes. The relevance of our findings to some rheological properties of the transient network is discussed in the concluding section.

2. Sticker Extraction Promoted by an External Force

In a recent work it was shown by Monte Carlo simulation that a chain in a grafted polymer layer (or polymer brush) cut off the wall is expelled from the brush in three steps.[14] In a first step, the cut end fluctuates and experiences many wall reflections. When its distance from the wall exceeds the grafting distance between chains (the blob size), ξ, the drift due to chain tension dominates the fluctuations and the chain contracts; the position of the cut end point is given by $z_0 \sim t^{1/2}$; in this second step, the chain is expelled by the osmotic pressure gradient in the grafted layer and the internal modes of the chain are irrelevant for the center of mass motion; the center of mass moves at a constant velocity $z_G \sim t$. In the third step, after the relaxation of all the internal modes, the cut end moves with the same constant velocity as the center of mass. These results are supported by a Rouse analysis and scaling arguments summarized now.

In the grafted layer, each chain can be decomposed into a sequence of blobs of size ξ given by the distance between grafting points, each blob containing $g \sim (\xi/b)^{1/\nu}$ monomers. b is the monomer size; ν is the swelling exponent which has the Flory value $\nu = 3/5$ in a good solvent and $\nu = 1/2$ in a Θ solvent. In the following, we often use a mean field theory which implicitly considers Gaussian chains $\nu = 1/2$.

The longest relaxation time of a chain in the grafted layer is the overall chain Rouse/Zimm relaxation time $T_r \sim \eta(N/g)^2\xi^d/k_BT$. In this expression d is the space dimension. For a polymer in a good solvent $d = 3$ and hydrodynamic interactions are screened over the blob size ξ, the friction over a chain segment of size ξ is then proportional to $\eta\xi$ where η is the solvent viscosity. In a general space dimension d, the friction on a chain segment of size ξ is proportional to $\eta\xi^{d-2}$; when $d = 4$ both hydrodynamic interactions and excluded volume are irrelevant; the scaling results for $d = 4$ correspond thus to a Gaussian chain with no hydrodynamic interactions (free draining limit) and can therefore be compared to the explicit mean field calculations with Rouse dynamics performed below.

The relevant length scale is the brush height $h \sim N\xi/g$. The scaling law for the average position of the chain end cut from the wall must be constructed from this scale and the macroscopic relaxation time: $\langle z_0\rangle = hf(t/T_r)$ where $f(x)$ is an unknown scaling function. In the tension driven regime where the fluctuations are small, the motion is dominated by local chain retraction, the law of motion is therefore independent of the chain contour length N and the N dependencies in h and T_r cancel each other out, this imposes $f(x) \propto x^{1/2}$. More precisely we obtain:

$$\langle z_0\rangle \sim \left(\frac{tk_BT}{\eta\xi^{d-2}}\right)^{1/2} \tag{1}$$

At short times, the motion of the end points is dominated by the fluctuations and is subdiffusive (as time goes on, internal modes with a longer wavelength are excited) with the usual Rouse/Zimm dynamic law:

$$\langle(z_0 - \langle z_0\rangle)^2\rangle \sim \left(\frac{k_BTt}{\eta}\right)^{2/d} \tag{2}$$

The deterministic motion driven by the chain tension is thus dominant when $t > \eta\xi^d/k_BT$, i.e., when $\langle z_0\rangle > \xi$; at larger distances from the grafting plane, the dispersion around the average position becomes negligible and the cut end is unlikely to come back to the grafting plane.

The motion of the chain center of mass out of the brush is driven by the osmotic pressure gradient that corresponds to a global force $\sim k_BT/\xi$ acting on the center of mass. The law of motion of the center of mass also follows a scaling law $\langle z_G(t)\rangle = hf_G(t/T_r)$. Equating the force and the friction of the chain section still trapped inside the brush, we obtain a constant velocity motion:

$$\langle z_G(t)\rangle \sim \frac{k_BT_g}{\eta N\xi^{d-1}}t \tag{3}$$

This corresponds to the short time limit $f_G(x) \sim x$. These results are in agreement with Monte Carlo simulations that use Rouse dynamics[14] and scaling arguments in Zimm dynamics.[15,16]

The same type of arguments can be applied to the expulsion of a chain cut from a spherical micelle (in the spherical geometry, we assume that $d = 3$ in this paragraph). The micelle has a core of radius R_c, which contains in our case the hydrophobic groups and contains f grafted chains i.e., f hydrophobic groups (Figure 2). The structure of the micelle corona is described by the Daoud-Cotton blob model and we restrict ourselves here to a good solvent. The distance between grafting points on the surface of the core is $\xi_c = R_cf^{-1/2}$. In the micelle corona, the chain structure is the same as in a semidilute solution but with a concentration that decays with the distance $r = R_c + z$ from the core center. The close packing of the blobs imposes a local correlation length $\xi(r) = rf^{-1/2}$. The total radius of the micelle scales as $R \propto N^{3/5}f^{1/5}$. Very close to the core surface $z < R_c$ the curvature effects are small and the structure is the same as that of a planar grafted layer. In particular, the very small time motion of the end point of a chain cut from the core which is a local process can be described by the same equations as in the planar geometry for the

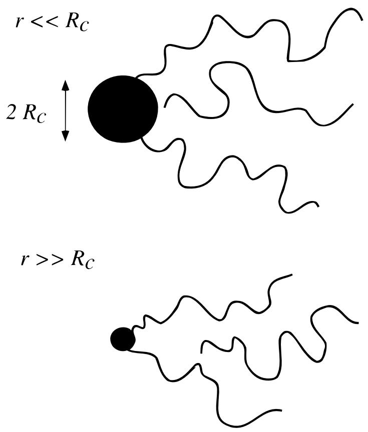

Figure 2. Expulsion of a chain from a spherical micelle. Only two arms and the expelled chain are represented. When the chain end is close to the core ($r \ll R_c$), the moving chain section sees a flat brush, for $r \gg R_c$ it sees a starlike brush.

average position of the end point and the fluctuations (eqs 1, 2) where the correlation length is ξ_c. This remains valid as long as the average distance of the end point from the core surface is smaller than the core radius i.e., at times $t < \eta R_c^3/(k_B T f^{1/2}) = t_c$. At later times, $r \gg R_c$, there is no scale in the problem and a power law is again anticipated for the average position of the end point $\langle z_0 \rangle$. The laws of motion for $z \gg R_c$ and $z \ll R_c$ crossover smoothly at time $t = t_c$, the law for $t > t_c$ is thus of the form $\langle z_0 \rangle = R_c(t/t_c)^{\alpha}$. As for $r \gg R_c$ the law of motion must be independent of R_c, we impose $\alpha = 1/3$. We thus find $\langle z_0 \rangle \simeq (k_B T f^{1/2} t/\eta)^{1/3}$. The motion of the center of mass can be studied using a similar argument. The displacement of the center of mass follows a scaling law $\delta r_G = \delta r_G(t_c)(t/t_c)^{\beta}$ where $N\delta r_G(t_c) = (\xi_c/b)^{2/3}\ R_c^2/b$ is obtained from the low r regime ($r \ll R_c$). As δr_G is independent of R_c for $t \gg t_c$ the powers of R_c have to cancel and $N\delta r_G = (tk_B T/6\pi\eta b^3)^{8/9} f^{1/9} b$. The center of mass velocity decreases then with time as $v_G = R/T_e(t/T_e)^{-1/9}$ where the expulsion time is $T_e = \eta R^3/f^{1/2} k_B T$. In the following, we study the extraction of a chain from the micelle; this is a very local process that occurs at the scale of the first blob ξ_c. We thus no longer consider curvature effects that are negligible and we limit ourselves to the flat brush geometry.

When an external force is applied to one chain end in a flat grafted layer (or to a vanishing fraction of chain ends) the overall brush structure is not changed. It is known, on the other hand, that exerting a pulling force on a finite fraction of chain ends causes the remainder of the brush to shrink mainly due to the osmotic pressure gradient established by the stretched chains. In the following, we neglect this shrinking and thus formally consider that a single chain is stretched.

We now consider explicitly a Rouse chain (with a finite tension applied to its free end point) in a flat polymer brush; we thus ignore here hydrodynamic interactions. At the mean-field level and within the strong stretching approximation,[17-19] the brush monomers experience a parabolic molecular potential $U(z) = A - (\pi^2 k_B T/8N^2 b^2) z^2$; the spring constant of the potential is chosen in such a way that any chain configuration reaches the grafting surface after N steps regardless of the free end position. The chemical potential per monomer A depends on the grafting density only: $A = \pi^2 k_B T h^2/8N^2 b^2$ where $h = ((12/\pi^2)\sigma_g b^2 v)^{1/3} N$ is the brush height, $\sigma_g = 1/\xi^2$, the grafting density and $v > 0$, the Edwards excluded volume parameter. When an extra tension τ is applied to a chain end, the chain stretches beyond the brush height h leaving only $\bar{n} < N$ monomers inside the parabolic potential in its optimal configuration. The optimal conformation (classical path) is obtained by solving Newton's law

$$\frac{k_B T}{b^2}\frac{\partial^2 z}{\partial n^2} = \frac{\partial U}{\partial z}$$

we find

$$h = \frac{2N\tau b^2}{\pi}\tan\left(\frac{\pi\bar{n}}{2N}\right) \tag{4}$$

$$z_n = \frac{2N\tau b^2}{\pi}\frac{\sin(\pi n/2N)}{\cos(\pi\bar{n}/2N)} \tag{5}$$

When the chain is cut off the wall the tension at the free end vanishes and the chain relaxes, the positions of the monomers inside the brush follow the Rouse equation

$$\zeta\frac{\partial z_n(t)}{\partial t} = \frac{k_B T}{b^2}\frac{\partial^2 z_n}{\partial n^2} + k_B T\left(\frac{\pi}{2Nb}\right)^2 z_n(t) + f_n(t) \tag{6}$$

where $\zeta = 6\pi\eta b^{d-2}$ is the monomer friction, the first term on the right-hand side describes the chain elasticity and the second one the interaction with the molecular potential; the last term is the Langevin random force. Note that the monomer size b used here is $b = b_{st}/\sqrt{3}$ where b_{st} is the polymer statistical segment as in most of the self-consistent grafted layer theories. The random force has a very short correlation time and obeys the standard fluctuation−dissipation theorem $\langle f_n(t)\rangle = 0$, $\langle f_n(t) f_m(t')\rangle = 2k_B T\zeta\delta_{m,n}\delta(t - t')$. The Rouse equation is supplemented by the boundary conditions:

$$\frac{\partial z_n}{\partial n}\Big|_{n=0} = 0\ (t > 0) \text{ at the cut end}$$

$$\frac{\partial z_n}{\partial n}\Big|_{n=\bar{n}} = \tau b^2/k_B T \text{ at the outer end} \tag{7}$$

In the optimal grafted configuration, $\bar{n}$ monomers are located inside the brush, and the remaining $N - \bar{n}$ monomers form an external strand of uniform tension τ. The transmission of the tension along an optimal path is given by the Hamilton invariant $\tau(z)^2 b^2/2k_B T - U(z)$; this gives the tension of the optimal path at the grafting surface $\tau_S = (\tau^2 + 2Ak_B T/b^2)^{1/2}$. The local structure of the stretched chain closest to the wall is isotropic over the correlation length $\xi_\tau = k_B T/\tau_S$ spanned by the contour length $g_\tau \sim \xi_\tau^2/b^2$. To avoid nonlinearities we ignore the external monomers and we impose a tension τ on the monomer $\bar{n}$ at $t > 0$, this is of course not rigorous but it is appropriate at the short time and length scales that we are interested in when the "information" about the cutting off the wall of the first monomer has not yet reached monomer $\bar{n}$. The Rouse equation giving the average position of monomer n, $\langle z_n(t)\rangle$, is solved in Laplace space by standard methods in Appendix A. The short time expansion for $\langle z_0(t)\rangle$ in direct space reads

$$\langle z_0(t)\rangle = 2\xi_\tau\left(\frac{t}{\pi\zeta\xi_\tau^{\,4}/(k_B T b^2)}\right)^{1/2} \tag{8}$$

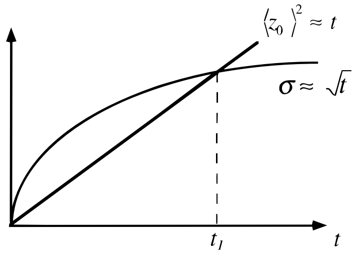

Figure 3. Statistics of the cut end position in a flat brush. The fluctuations become negligible for $t > t_1$ where the cut end retracted, on average, over more than one correlation length.

where we have adopted the precise definition $\xi_\tau = k_BT/\tau_S$. Note that eq 8 involves only local space and time scales: the local correlation length ξ_τ and the Rouse time associated with the contour length g_τ. It is very similar to eq 1 where the distance between grafting points has been replaced by the correlation length ξ_τ and $d = 4$. The fluctuation of $z_0(t)$ around its average value $\langle z_0(t)\rangle$ is characterized by the variance $\sigma(t) = \langle(z_0(t) - \langle z_0(t)\rangle)^2\rangle$. The mean-square fluctuation $\sigma(t)$ can be calculated from the Rouse equation with a boundary condition of vanishing tension fluctuation at both chain ends, $n = 0$ and $n = \bar{n}$. It is thus the same as for a chain cut off the wall in the absence of tension[14] (see also the appendices). In the short time limit

$$\sigma(t) = \left(\frac{8tb^2k_BT}{\pi\zeta}\right)^{1/2} \tag{9}$$

This is independent of the overall chain length as expected. Fluctuations are unlikely to bring the cut end back to the grafting surface when $\langle z_0(t)\rangle > \sqrt{\sigma(t)}$ (Figure 3). This occurs when $t > t_1$ with

$$t_1 = \frac{\zeta\pi b^2}{2k_BT}\left(\frac{k_BT}{b\tau_S}\right)^4 \tag{10}$$

The time t_1 is proportional to the Rouse time associated with the contour length g_τ of a correlation volume. Up to the change in the correlation length, these results are similar to the scaling results presented above, with $\nu = {}^1/_2$ and $d = 4$. There are clearly two limiting cases: (i) if $\tau^2 > Ak_BT/b$, the applied tension monitors the retraction and the time t_1; (ii) if $\tau^2 < Ak_BT/b$, the typical tension of a grafted brush chain close to the wall dominates the applied tension. The average distance from the surface at time t_1 is proportional to the correlation length of the stretched chain closest to the wall ξ_τ:

$$\langle z_0(t_1)\rangle = \frac{\sqrt{2}b}{\tau_Sb/k_BT} \tag{11}$$

We now turn to the case where the grafted chains stick to the wall by a small end group trapped in an attractive surface potential of microscopic width b. Here we assume the Zimm dynamics and $2 < d \le 4$. Following the previous discussion, the escape time T_- of interest is the first passage time of the sticking group at a few correlation length ξ_τ from the wall. At distances $z > \xi_\tau$, the sticking group is unlikely to fluctuate back to the wall and to readsorb and the desorption is effective. Here we give a simple scaling argument to find the first passage time T_- and postpone a detailed derivation to the next section where a more realistic situation is considered. The qualitative argument is similar to the classical Kramers argument for a pointlike Brownian particle.[20,21] The sticker is bound by the microscopic surface potential where its fluctuations are mainly restricted to a width b. The probability distribution law of the sticker in the potential is essentially thermalized; it is given by Boltzmann's law: $P(z) \sim b^{-1} \exp(-E(z)/k_BT)$ up to the top of the potential barrier where the sticker escapes by fluctuation. To estimate the first passage time at $z = \xi_\tau$ we calculate the outward flux of the sticker with the boundary conditions that the probability $P(z)$ is thermalized up to within k_BT of the top of the surface potential and vanishes at $z \sim \xi_\tau$. The surface potential being very steep, the probability roughly decreases over the distance ξ_τ and $\partial P/\partial z \sim -b^{-1} \exp(-E)/\xi_\tau$, where E is the desorption energy of the sticker. The main problem is that of the relevant friction linking the probability gradient to the probability flux. Here we argue, as suggested by the study of the expulsion of a non adsorbing end point, that it is sufficient to move a chain section of radius ξ_τ during this escape process, the relevant friction is thus $\sim\eta\xi_\tau^{d-2}$. The outward flux J_- is then given by $J_- \sim k_BT\exp(-E/k_BT)/\eta b\xi_\tau^{d-1}$. The typical extraction time T_- is obtained as $1/J_-$:

$$T_- \sim \frac{\eta b\xi_\tau^{d-1}\exp(E/k_BT)}{k_BT} \tag{12}$$

Note that the preexponential factor is slightly different from the one obtained in reference 14 where the local friction was chosen rather arbitrarily. The adsorbed sticker fluctuates in the surface potential and over the first correlation length. Our simple analysis requires that the sticker is bound by the surface potential. There is however an entropic penalty $\log(\xi_\tau/b)$ for the sticker to be located in the narrow potential well; the surface potential binds the sticker only if $E/k_BT > \log(\xi_\tau/b)$; in the other limit, the time T_- is equal to a typical diffusion time over the first correlation length $\eta\xi_\tau^d/k_BT$. In this simple picture, the activation energy is not decreased by the work of the chain tension while the sticker is moving out of the potential sink as long as $\tau_Sb < k_BT$. The main effect of the external tension is thus to reduce the correlation length down to ξ_τ and hence to accelerate the chain extraction. In the following, we consider finite size stickers: the finite size of the stickers has two main consequences: a significant decrease of the activation energy at high applied tensions and a change in the friction for the chain passing through the potential barrier; at high tension it becomes equal to the sticker friction.

3. Finite Sticker Size Effects

In practical cases, stickers are short chain sections that have a certain rigidity. We consider here the two extreme limits of rigid stickers modeled as small rods and liquid stickers modeled as a small flexible polymer chain in a very poor solvent.

3.1. Rigid Sticker. We first discuss the limiting case of a completely rigid sticker pictured as a rod of length L, thickness b, and friction coefficient ζ'. The sticker is linked to the stretched chain of contour length N, the other chain end being fixed at position z_b in order to impose a finite tension $\tau = z_b/Nb^2\ k_BT$ on the chain; $z_b \gtrsim R_0 = N^{1/2}b$. In the following we only consider translational motions of the sticker and characterize its position by that of the junction point with the chain. The sticker experiences a potential $U(z)$ minimum at $z = 0$ reflecting the short range interactions between sticker and solvent. In a first step, we want to understand qualitatively how the spring constant of the potential, the chain elasticity, the sticker friction, and the friction of the internal chain modes influence the extraction time T_-. To build up our scaling arguments on a sound basis, we explicitly consider the case of a parabolic potential $U(z) = kz^2/2$ that allows for explicit calculations. As we already know that the effect of other chains in the grafted layer merely amounts to a change in the relevant extraction tension, we restrict ourselves to a single chain; hence $\tau_S = \tau$ in section 3. We first characterize the statistics of $z_0(t)$ for the isolated stretched sticking chain before calculating the first passage time T_- of the sticker at position L. The arguments are then generalized to more realistic potentials. These calculations also give some support to the scaling arguments presented in the previous section.

The statistics of the sticker position in a parabolic potential $z_0(t)$ are governed by the Rouse equation:

$$\zeta \frac{\partial z_n}{\partial t} = \frac{k_B T}{b^2} \frac{\partial^2 z_n}{\partial n^2} + f_n \tag{13}$$

At the fixed end of the chain, $z_n = z_b$. The force balance on the $n = 0$ monomer (the sticker) is written as

$$0 = -\zeta' \frac{\partial z_0(t)}{\partial t} + \frac{k_B T}{b^2} \frac{\partial z_n(t)}{\partial n}|_{n=0} - k z_0(t) \tag{14}$$

To respect the fluctuation dissipation theorem the Langevin force must satisfy $\langle f_n \rangle = 0$, $\langle f_n(t) f_m(t') \rangle = 2k_BT\delta(n - m)\delta(t - t')(\zeta + \zeta'\delta(n))$. This can be explicitly checked by considering a chain of discrete monomers attached to the sticker. The average sticker position $\langle z_0(t) \rangle$ and the fluctuation $\sigma = \langle(\langle z_0(t)\rangle - z_0(t))^2\rangle$ are calculated by standard methods in Laplace space, s being conjugated to the time t in Appendices A and B.

$$\langle z_0(s) \rangle = \frac{z_b}{Ns} \frac{1}{\dfrac{\zeta' b^2 s}{k_B T} + \dfrac{b^2 k}{k_B T} + \sqrt{\dfrac{b^2 \zeta s}{k_B T}} \coth\left(\sqrt{\dfrac{b^2 \zeta s}{k_B T}} N\right)}$$

$$\sigma(s) = \frac{b^2}{s} \frac{1}{\dfrac{\zeta' b^2 s}{2k_B T} + \dfrac{b^2 k}{k_B T} + \sqrt{\dfrac{b^2 \zeta s}{2k_B T}} \coth\left(\sqrt{\dfrac{b^2 \zeta s}{2k_B T}} N\right)} \tag{15}$$

This calculation assumes that at time $t = 0$, the sticker starts at the bottom $z = 0$ of the potential and that the chain is in its optimal configuration (uniform tension).

The chain retraction when the sticker does not feel the parabolic potential can be discussed by setting $k = 0$. At long times $t > T_R$, where $T_R = N^2\zeta b^2/k_BT$ is the Rouse time that we suppose to be the longest relaxation time in the problem, we recover the equilibrium results, $\langle z_0(t) \rangle = z_b$, $\sigma = Nb^2$. At short times, the retraction is dominated by the sticker, the sticker moves under the effect of the chain tension $\langle z_0(t) \rangle = (k_BTz_b/Nb^2\zeta')t$ and the fluctuation is given by the sticker diffusive motion $\sigma(t) = (2k_BT/\zeta')t$. As time goes on, however, Rouse modes of longer wavelength are excited and the chain friction becomes dominant for $t > t_1 = (b^2/k_BT)(\zeta'^2/\zeta)$. The regime where the chain dominates the friction, which has been discussed in the previous section, is of course only found for $t_1 < T_R$, when the sticker friction is smaller than the total chain friction. The conclusions of the previous section that the fluctuations are negligible for sticker extraction and thus that the sticker does not fluctuate back to the wall as soon as it has crossed a few chain correlation lengths ξ_τ still holds true, but the relevant friction is the largest of the sticker friction and the correlated chain section friction.

We now discuss the sticker behavior in the parabolic potential. At times larger than the Rouse time, the sticker position $z_0(t)$ reaches its equilibrium statistics with $\langle z_{0,eq} \rangle = \tau/(k + (k_BT/Nb^2))$ and fluctuations $\sigma_{eq} = k_BT/(k + (k_BT/Nb^2))$. They correspond to the motion of a particle attached between two springs of spring constants k (the potential) and k_BT/Nb^2 (chain elasticity). At times shorter than the Rouse time the sticker relaxes under the action of the constant applied tension $\tau = z_bk_BT/Nb^2$ but the chain can be considered as infinite and the coth in eq 15 can be considered as equal to unity. The sticker has then a pseudo-equilibrium position $\langle z_0 \rangle = \tau/k$, and the relevant spring constant for the fluctuations is k. This pseudo-equilibrium state is reached provided that the characteristic relaxation times discussed below are all smaller than the Rouse time. The statistics of the sticker coordinate z_0 depend on the behavior of the denominator of eq 15 where the coth equals unity. If $1 - 4(b^2k/k_BT)(\zeta'/\zeta) < 0$, the denominator has no real root and the statistics are dominated by the sticker from short times to the pseudo-equilibrium. This criterion can also be written as $4\zeta' > g_k\zeta$ where $g_k = k_BT/kb^2$ is the contour length spanning the typical pseudo-equilibrium fluctuation of the sticker. For smaller sticker frictions ζ' however the statistics are only dominated by the sticker at short times $t < t_1 = \zeta'^2b^2/k_BT\zeta$ where the activated chain friction is lower than the sticker friction. At longer times, the chain friction dominates and the pseudo-equilibrium in the potential is reached for $t > t_2 = k_BT\zeta/k^2b^2$. Our qualitative argument assumes for simplicity that the time scales are well separated and we do not give detailed expressions of the relaxation functions as they are strongly potential dependent.

If we assume that the random forces $f_n(t)$ are Gaussian then the random variable $z_0(t)$ is also Gaussian and its probability distribution $G(z_0,t)$ is completely determined by the two first moments given in eq 15.

$$G(z_0,0|t) = \frac{1}{\sqrt{2\pi\sigma}} \exp - \frac{(z_0 - \langle z_0(t) \rangle)^2}{2\sigma(t)} \tag{16}$$

The propagator $G(z_0,z_{0i}|t)$ gives the probability density for the sticker to be at z_0 after a time t given it started at z_{0i} at time 0 with the chain in its optimal configuration. In the following we use only this type of propagators and thus formally reduce the rather complex chain+sticker problem to a single particle problem.

We can now discuss the escape of the sticker from the parabolic potential. The potential must be cut at $z = L$, allowing for the sticker to escape (Figure 4). The first passage propagator $G_f(L,0|t)$ at $z_0 = L$ is of special interest as it gives the probability density (frequency) for the sticker starting at the bottom of the potential $z = 0$ to reach $z = L$ for the first time at time t. The sticker located at $z = L$ at time t crossed that position for the

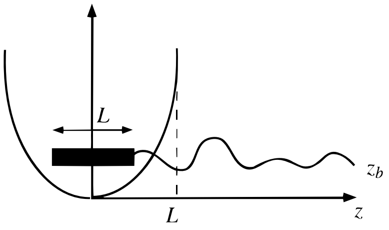

Figure 4. Parabolic potential cut at $z = L$.

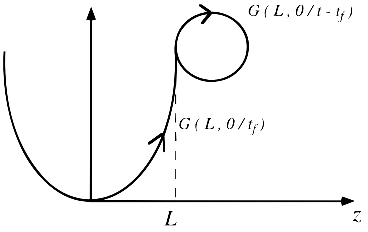

Figure 5. First passage propagator and its link to free propagators. The end found at position $z = L$ at time t first reached this position at $t_f < t$ and went for a extra loop bringing it back to $z = L$ at time t.

first time at time $t_f \leq t$ and made an extra loop bringing it back to L after a (maybe vanishing) time $t - t_f$ (Figure 5). This can be cast in a time−convolution equation, which is readily solved using the Laplace variable conjugate to time:

$$G_f(L,0|s) = \frac{G(L,0|s)}{G(L,L|s)} \tag{17}$$

where s is the Laplace variable conjugated to time. The simple form of G_f is a direct consequence of the fact that we use Gaussian propagators with specified initial chain configurations. This is a standard assumption, used by several authors.[22−24] Another approach is to use thermalized initial conditions.[25] As we will see our approach yields results in agreement with reasonable qualitative arguments. The mean first passage time $T_-(L)$ is the first moment of $G_f(L,0|t)$; it is obtained from the small s expansion of $G_f(L,0|s)$, $G_f(L,0|s) = 1 - T_-(L)s + ...$ Because of the existence of an equilibrium state the Gaussian propagators have singular Laplace transforms at $s = 0$, $G(f,i|s) = G_{eq}(f)\, s^{-1} + ...$, G_{eq} being the equilibrium distribution in the parabolic potential. Extracting the singular part of the Gaussian propagators we obtain:

$$T_-(L) = \frac{1}{G_{eq}(L)} \int_0^\infty \mathrm{d}t\, (G(L,L|t) - G(L,0|t)) \tag{18}$$

The integral is now well behaved. The calculation of the loop propagator $G(L,L|t)$ parallels that of $G(L,0|t)$, the average position $\langle z_0(t)\rangle_L$ of a sticker starting at L at time 0 is

$$\langle z_0(t)\rangle_L = L + \langle z_0(t)\rangle\, (1 - L/z_{0,eq}) \tag{19}$$

The two average positions $\langle z_0\rangle$ and $\langle z_0\rangle_L$ are thus governed by the same relaxation function. We now focus on the case where the activation energy is much larger than k_BT. The integral giving the first passage time eq 18 is then dominated by the loop propagator, similar conclusions are reached in Appendix C following a slightly different route. The main contribution to the loop propagator integral involves the sticker friction for $(\zeta'/\zeta)b^2(L/(\delta X)^2)^2 > 1$ where $k(\delta X)^2 = k_BT$ and the chain friction otherwise. This criterion has simple physical meaning: it compares the friction of the sticker ζ' to that of the chain section spanning the width $D = (\delta X)^2/L$ of the potential barrier build when the parabolic potential is cut at L (Figure 6a). In the sticker dominated regime that corresponds to a narrow barrier and/or large sticker, the result for a particle in a parabolic potential is recovered. In the chain dominated regime, the friction ζ' is replaced by the friction $\sim \zeta D^2/b^2$ of the typical chain section spanning the width of the barrier D. More precisely, we obtain:

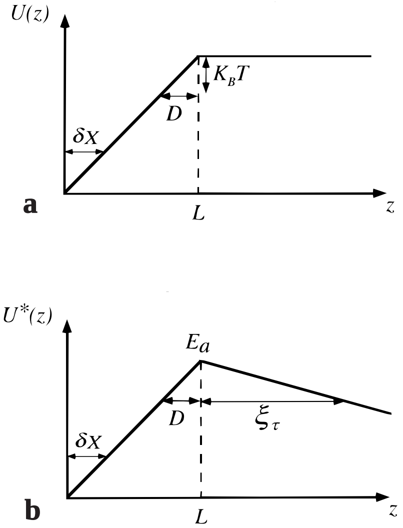

Figure 6. (a) A more realistic sticker potential. (b) Effective potential U^*.

$$T_-(L) = (2\pi)^{1/2}\, \frac{\zeta'}{k_BT}\, \delta X_e\, \frac{(\delta X)^2}{L} \exp(E_a/k_BT) \text{ (sticker)}$$

$$T_-(L) \simeq \pi^{3/2}\, \frac{\zeta}{k_BT}\, \delta X_e\, \frac{(\delta X)^2}{L} \left(\frac{(\delta X)^2}{bL}\right)^2 \exp(E_a/k_BT) \text{ (chain)} \tag{20}$$

$\delta X_e = \sqrt{\sigma_{eq}}$ is the rms fluctuation of the sticker position at thermal equilibrium. Below we assume that the spring constant k is much larger than the chain elasticity constant k_BT/Nb^2; hence $\delta X_e \simeq \delta X$. The activation energy $E_a = (L - \langle z_{0,eq}\rangle)^2\, (k + k_BT/Nb^2)/2$ accounts for the spring constant of the chain and for the relaxation of chain elastic energy when the sticker moves from its equilibrium position to $z = L$. Substituting $\langle z_{0,eq}\rangle = \tau/(k + k_BT/Nb^2)$ in the last equation for E_a and taking into account that $k_BT/Nb^2 \ll k$, we get $E_a \simeq (k/2)(L - \tau/k)^2$. Of course we assume that

$$\tau/k < L \tag{21}$$

as otherwise the chain tension would readily pull the sticker out of the core. The first passage time formulas have a simple physical meaning: The sticker typically fluctuates around its equilibrium position over a width $\delta X_e \simeq \delta X = (k_BT/k)^{1/2}$, its equilibrium probability distribution in the parabolic potential is $G_{eq} \sim \exp(-E)\delta X_e^{-1}$. With the potential cut at $z = L$ where the activation energy E_a is much higher than k_BT, the distribution is thermalized up to within k_BT from the top of the barrier. The probability $P(z)$ of finding a sticker that did not yet visit $z = L$ vanishes over the width D of the barrier. The relevant probability gradient is $\nabla P \sim -\exp(-E_{a})(D\delta X_{e})^{-1}$. The outward flux $J_{-} \sim -\zeta^{*}\nabla P$ depends on whether the friction ζ^{*} over a distance D is dominated by ζ' or by the Rouse friction $\sim \zeta D^{2}/b^{2}$ of the chain section spanning D. Similar arguments were anticipated in Section 2, where the sticker friction was neglected.

The sticker potential in our case is certainly not parabolic and it is rather steep, its width D is typically comparable to the monomer size. However, the sticker cannot be considered as extracted after leaving the interface; as we know from Section 1, it has to move away from the interface by the local chain correlation length ξ_{τ}. The relevant time is therefore the first passage time at this position, the previous arguments still apply but we must replace the width of the barrier D by the distance $D + \xi_{\tau}$. Note that $D = k_{B}T/kL < \xi_{\tau} = k_{B}T/\tau$ since $\tau < kL$ (see eq 21); therefore, the width of the barrier $D + \xi_{\tau} \sim \xi_{\tau}$. The effective friction constant is $\zeta^{*} = \zeta' + \zeta_{chain}$ where ζ_{chain} is the friction constant of the chain section spanning $D + \xi_{\tau} \sim \xi_{\tau}$: $\zeta_{\mathrm{chain}} \sim \zeta\xi_{\tau}^{2}/b^{2}$. The extraction time under the constant tension τ is thus

$$T_{-} \sim \frac{\zeta^{*}}{k_{B}T}\delta X \xi_{\tau} \exp(E_{a}/k_{B}T) \qquad (22)$$

where $\zeta^{*} \sim \zeta' + \zeta\xi_{\tau}^{2}/b^{2}$ and $\delta X = (k_{B}T/k)^{1/2}$. Hence the criterion determining the sticker dominated regime is $\zeta' b^{2}/\zeta\xi_{\tau}^{2} \gtrsim 1$. Rapid extraction occurs only at high tensions where the chains have a nonlinear elasticity, the sticker friction is in this case dominant.

Our result for the extraction time has been obtained ignoring hydrodynamic interactions. It is however difficult to explicitly treat hydrodynamic interactions in details close to the interface. For our purpose it is sufficient to treat hydrodynamic interactions at the scaling level. This amounts to change the relevant chain friction from the Rouse value $\zeta\xi_{\tau}^{2}/b^{2}$ by the Zimm non draining value $6\pi\eta\xi_{\tau}$ (the numerical factors such as 6π are omitted below); the sticker friction is $\zeta' \sim \eta L$ (creeping rod). Hence $\zeta^{*} \sim \zeta' + \eta(D + \xi_{\tau}) \sim \eta(L + \xi_{\tau})$, and so the sticker-dominated regime is given by $L \gtrsim \xi_{\tau}$, a criterion directly comparing the sticker size and the surface correlation length. (Note that D is negligible in comparison with L since $E_{a} \gg k_{B}T$.)

The parabolic potential has allowed us explicit calculations and then the construction of heuristic arguments in agreement with these detailed calculations. It is however not realistic. When the sticker is pulled out into the solvent, the energy penalty is proportional to the pulled length that is directly exposed to the solvent. Small sticker fluctuations with respect to other close stickers in the interface are less easy to model, in any case we expect these fluctuations to be of order b if the contact energy between a monomer and the solvent is of order $k_{B}T$. We propose the following sticker potential:

$$U(z) = +\infty \ (z < 0) \qquad U(z) = k_{B}T\,\epsilon z/b \ (0 < z < L)$$
$$U(z) = k_{B}T\epsilon L/b \ (z > L) \qquad (23)$$

with $\epsilon k_{B}T$ the energy penalty for exposing one sticker monomer to the solvent. Our heuristic derivation can still be used for this potential and the extraction time is given by eq 22 with $D = b/\epsilon$, $\delta X = b/\epsilon$, and $E_{a} = L(k_{B}T\epsilon/b - \tau)$. When hydrodynamic interactions are taken into account, the Zimm value of the friction should be substituted in the chain dominated regime. An equivalent method to obtain these results is an adapted Kramers formula[21] where the friction is set to $\zeta^{*} \sim \zeta' + \eta(D + \xi_{\tau}) \sim \eta(L + \xi_{\tau})$ and the chain is replaced by a constant force acting on the sticker corresponding to an energy: $U^{*} = U - \tau z$ (Figure 6b).

$$T_{-} = \int_{0}^{\infty} \mathrm{d}z\, \zeta^{*}\exp(U^{*}(z)) \int_{0}^{z} \mathrm{d}z' \exp(-U^{*}(z')) \qquad (24)$$

So far we did not explicitly account for the impenetrable wall constraint. At equilibrium, the partition function of a chain with its end at a distance $z < \xi_{\tau}$ from the wall is reduced by a factor $(z/\xi_{\tau})^{(\gamma_{1}-\gamma)/\nu}$. The critical exponents are approximated by $\gamma \approx 1.165$, $\gamma_{1} \approx 0.676$ where the latter is obtained by interpolation between a first order ϵ-expansion and the exact 2D result.[28] Inside the first correlation length ξ_{τ} the chain is thus stretched with an additional local structure (neighboring chains do not overlap) corresponding to local stretching. Formally the minimum of the sticker potential moves to $z = D(\gamma - \gamma_{1})/\nu$ a distance from the wall comparable to the sticker equilibrium fluctuations. The additional stretching energy can be relaxed during extraction. The stretching energy stored in the section extending between D and z is of order $(\gamma/\nu - \gamma_{1}/\nu)$ log z/D (this result holds for Gaussian chains where chain sections are not correlated, we expect it to hold for excluded volume chains as the change in chain free energy when the sticker moves outward from D to z merely arises from the chain section spanning a distance $\sim z$).

When the sticker is larger than ξ_{τ} the impenetrable wall constraint reduces the potential barrier by the relaxed elastic energy $k_{B}T(\gamma/\nu - \gamma_{1}/\nu)$ log ξ_{τ}/D, this causes the extraction time to decrease by a factor $(D/\xi_{\tau})^{(\gamma-\gamma_{1})/\nu}$.

In the chain dominated regime ($\xi_{\tau} > L$), the situation is more complicated. The potential barrier is only decreased by $k_{B}T(\gamma/\nu - \gamma_{1}/\nu)$ log L/D. Formally the extracted chain can release a few $k_{B}T$ elastic energy while retracting over several times L, the actual width of the effective barrier would then rather be L and not the larger ξ_{τ}. The length L of the sticker would replace ξ_{τ} and an additional factor $(D/L)^{(\gamma-\gamma_{1})/\nu}$ account for the reduction of the barrier. However, the energy relaxed upon retraction only increases as $(\gamma/\nu - \gamma_{1}/\nu)$ $\log(z/L)$ within the thermal blob and in practice retraction over a few thermal blobs may be required to ensure irreversible extraction ($(\gamma/\nu - \gamma_{1}/\nu)$ $\log(\xi_{\tau}/L)$ is unlikely to be much larger than one).

These results are valid if the activation energy E_{a} is large, i.e., if the chain tension is smaller than the critical value $\tau_{c} = \epsilon k_{B}T/b$. If the tension gets larger, the extraction of the sticker is not thermally activated.

3.2. Flexible Sticker. Flexible stickers can be modeled by a flexible chain of n monomers in a very poor solvent. In that case, the hydrophobic core of the micelles is a collapsed region where the chain connectivity does not play an important role and it can be viewed at as an ordinary liquid drop at large scales with a correlation length ξ_{th} in the mesoscopic range. In the standard scaling theory of polymers in poor solvents, the thermal correlation length is inversely proportional to the distance t to the Flory compensation temperature, $t = -v/w$, where v and w^{2} are the second (the negative excluded volume) and the third effective virial coefficients between monomers respectively: $\xi_{\mathrm{th}} \sim b/t$. The free energy of the collapsed core is dominated by interfacial energy with a macroscopic surface tension between the polymer and the solvent $\gamma \sim k_BT(b/w)t^2$.[26] However for very poor solvents, as we may consider here, there is hardly any solvent mixed with the polymer and the correlation length is almost the monomer size, in that case the surface tension is $\gamma \sim k_BT/b^2$. In the following we keep both ξ_{th} and γ as given quantities and we do not try to express them in terms of temperature.

During the extraction, the sticker forms an almost spherical globule of volume $V = 4\pi/3\ R^3 \simeq n/c$, with a monomer density c very close to that of the dense sticker phase at equilibrium with the solvent ($c = t/w$ in the scaling theory). The globule size L in the direction of extraction is then $L \simeq 2R$. Only at very high tensions τ would L strongly depart from the spherical globule diameter $2R$; this would occur when the work associated with the tension is larger than the interfacial energy $2\tau R > 4\pi\gamma R^2$, i.e., $\tau > \tau_0 = 2\pi\gamma R$. It is known however that way below this threshold, at a critical tension τ_c the collapsed globule of radius R discontinuously stretches and reaches the configuration of a stretched Gaussian chain which is equivalent to a cylinder of radius ξ_τ and of length $L_c \simeq V/(\pi\xi_{th}^2)$. The critical tension $\tau_c = 2\pi\gamma\xi_{th}$ when chain extraction can be achieved without any activated state is much lower than τ_0. It is thus sufficient to describe the activated state as a spherical globule with activation energy $E_a^{(sph)} = 4\pi\gamma R^2 - 2\tau R$ at tensions smaller than this critical value.

Generally speaking, one can think of two activated states: the spherical globule just discussed and the extended cylinder of radius ξ_{th} and activation energy $E_a^{(cyl)} = (\tau_c - \tau)L_c$; the actual activation energy can be taken as the minimum of the activated energies for spherical and cylindrical activated globule:

$$E_a = \min[4\pi\gamma R^2 - 2\tau R, (\tau_c - \tau)L_c] \qquad (25)$$

At low tensions, the spherical globule is the relevant activated state. Very close to the critical tension $\tau_c = 2\pi\gamma\xi_{th}$ where the activation energy vanishes, the activated state jumps from almost spherical to cylindrical with radius close to ξ_{th}; at higher tensions the activation energy decreases linearly with tension and vanishes. Close to the critical tension our macroscopic description of the activated state (i.e., the picture of a large globule) breaks down as the radius of the cylindrical extracted globule becomes comparable to the correlation length ξ_{th}.

A more precise description of the activated state far from τ_c can be obtained by solving the problem of an axisymmetric drop under end tension (this is formally similar to a drop around a thin fiber[27]). The main conclusions are: the globule remains almost spherical throughout; when the deformation of the micelle core between two activated globules corresponding to two stretched chains is taken into account, the activation energy of each globule is unaffected in the large core limit; the activation energy of the extrapolated elongated globule crosses that of the cylindric globule of radius ξ_{th} at about $1 - \tau/\tau_c = {}^3/_2(\xi_{th}/R - (\xi_{th}/R)^2)$ as would follow from the simple spherical model discussed above. This certainly does not describe the crossover from activated to direct extraction accurately but the idea of a sharp transition very close to τ_c for large globules seems reliable: the crossover tension to an extended activated volume can be qualitatively looked at as the tension for unwinding the (smaller) spherical activation volume.

We now write the extraction time using a Kramers-like approach in the limit of high activation barrier, E_a, as defined in eq 25. It is more difficult to construct the scaling form of the preexponential time. Choosing again the position of the junction point between the chain and the sticker as a reaction coordinate, the typical equilibrium fluctuations extend over the correlation length ξ_{th}. Hence the probability density at the top of the barrier is $\sim\exp(-E_a/k_BT)/\xi_{th}$. The junction point has to cross the first chain correlation length ξ_τ in order to be extracted. The relevant friction ζ^* in this process is the largest of the globular sticker friction $6\pi\eta R$ and of the friction of a chain section spanning the chain correlation length $6\pi\eta\xi_\tau$: $\zeta^* \sim \eta(R + \xi_\tau)$. (We use here the Zimm dynamics that takes into account the hydrodynamic interactions.) We thus propose:

$$T_- \sim \xi_{th}\xi_\tau \frac{\zeta^*}{k_BT} \exp(E_a/k_BT) \qquad (26)$$

4. Application to Physical Gels

In this paper, we have studied the extraction process of a hydrophobic sticker from a hydrophobic domain in a telechelic polymer gel. Our results rely on a Rouse analysis of chain retraction when the sticker has been expelled from the aggregate and on an analysis of the first passage statistics for the sticker initially trapped in a potential sink reflecting the preference of hydrophobic/hydrophilic junction point for the interface.

Chain extraction becomes irreversible when the chain has retracted over a few extra correlation lengths after the sticker has left the aggregate. As curvature effects do not play an important role for the extraction process from the core of a flower micelle in the telechelic gel, it is simpler to consider a flat geometry in which explicit calculations are possible. The relevant local correlation length ξ_τ decreases with the applied tension, $\xi_\tau = k_BT/\tau_S = k_BT(\tau^2 + 2Ak_bT/b^2)^{-1/2}$ where the monomer chemical potential A in the brush is proportional to the square of the typical tension of a free brush chain.

The statistics of the sticker inside a potential sink mimicking the interface is dominated by the sticker friction at short times and if the fluctuations are large enough by the friction of the chain section spanning the fluctuations at larger times. From the statistics of the sticker in the potential we construct the first passage statistics at a non equilibrium position. The mean first passage time at a position far from equilibrium is qualitatively given by an argument very similar to the classical Kramers' argument. However the relevant friction is the largest of the sticker friction or the friction of the typical chain section spanning the fluctuations around the final position. The activation energy is also reduced due to the relaxation of the chain elastic energy when the sticker moves up hill in the potential.

Combining these two results we obtain an extraction time that strongly depends on chain tension provided the tension is larger than the typical tension in the polymer brush. At moderate tensions, the extraction time decreases as a power law with increasing tension, at somewhat higher tension where the tensile blob becomes shorter than the sticker, the power law is weaker but it is dominated by a strong exponential decrease of the activation energy. Eventually, for high tension the activation energy becomes irrelevant and extraction is no longer thermally activated.

Similar conclusions were reached in the case where the hydrophobe is a flexible polymer block. However, the determination of the activation energy is rather subtle in that case. A stretched polymer strand can be extracted from the dense phase, without activation, under a critical force $\tau_c \sim \gamma\xi_{\rm th}$. If the tension is lower than this critical value, extraction is an activated process. As the sticker is deformable, the shape of the sticker in the activated state must be determined. The activated globule remains almost spherical at low tensions, up to the vicinity of the critical tension for extraction. The activated state jumps from an almost spherical shape to an extended cylinder of radius $\sim\xi_{\rm th}$ at a value τ close to the critical tension for extraction from the micelle core, $\tau \simeq \tau_c(1 - \xi_{\rm th}/R)$. At higher tensions, the activation energy decreases linearly with tension and vanishes at the critical tension.

Several rheological effects observed in telechelic polymer gels are related to the relaxation of hydrophobic domains under constraint. In the following, we focus on gels obtained from hydrophilic polymers with hydrophobically modified ends and consider for the purpose of the discussion, the case of rodlike stickers.

When an external stress is applied to the gel, the gel deforms elastically at times shorter than the debridging time T_- calculated in this paper. At larger times the bridges and loops reorganize and the gel flows. The system is thus shear thinning with time.

At concentrations well above the flower micelle overlap concentration, the viscosity is controlled by the deformation energy barrier to be overcome for a micelle to move across its next neighbor shell $U_{\rm def}$, and by the activation energy for sticker extraction B; log $\eta \sim U_{\rm def} + B$. For large strain $\gamma > 1$, the barrier against motion of a debridged micelle becomes irrelevant; this occurs roughly for $\sigma/\mu > 1$ where μ is the shear modulus of the gel of the order of the elastic energy density and σ the applied stress. This corresponds to a first shear thinning of the gel. At higher applied stress the viscosity essentially depends on the activation energy for sticker extraction that decreases with bridge tension and thus with applied stress as discussed previously. The decrease of B causes a second shear thinning of the gel.

In some experiments, a shear thickening of the gel at concentrations weakly below the flower micelle overlap concentration is also observed. The viscosity is known to sharply increase when the overlap concentration

$$\phi^* = \left(\frac{f^{1/(d-1)}}{N_{\rm B}}\right)^{d\nu-1}$$

is reached from below. The overlap concentration is decreasing with decreasing aggregation number. It is thus tempting to explain the shear thickening by a decrease of the aggregation number under shear resulting in a lower ϕ^*. The overlap concentration ϕ^* would then be crossed at constant solution concentration, the system would bridge and the viscosity be enhanced. An easier way of testing this scenario is to study the steady-state aggregation number of a single micelle in a shear flow. This however remains a somewhat controversial issue. A detailed calculation by Jones et al.[29] based on pseudo-free-energy arguments would rather predict an increase of the aggregation number in weak shear flow. The physics behind their result is that the chains in aggregates are less exposed to the flow and thus less stretched, hence they should aggregate more in the flow, following a "minimum energy" argument. Some recent experiments using fluorinated stickers[31] or ionomers[32] have shown shear thickening related to nonlinear chain elasticity. This behavior is to be expected for systems with high critical tension.

These considerations on the gel nonlinear rheology are rather qualitative but we hope to present a more quantitative description in a future work.

Appendix A. Calculation of Mean Values by Laplace Transformation

We start with the case of a chain in a flat polymer brush under external tension, which is cut off the grafting surface (Section 2, main text). From the Rouse equation eq 6 we obtain the equation for the average position of monomer n

$$\zeta\,\frac{\partial\langle z_n(t)\rangle}{\partial t} = \frac{k_{\rm B}T}{b^2}\,\frac{\partial^2\langle z_n\rangle}{\partial n^2} + k_{\rm B}T\left(\frac{\pi}{2Nb}\right)^2\langle z_n(t)\rangle \qquad (27)$$

with the following boundary conditions:

$$\begin{aligned}\frac{\partial\langle z_n\rangle}{\partial n}\Big|_{n=0} &= 0\ (t > 0)\ \text{at the cut end}\\ \frac{\partial\langle z_n\rangle}{\partial n}\Big|_{n=\bar{n}} &= \tau b^2/k_{\rm B}T\ \text{at the outer end}\end{aligned} \qquad (28)$$

After Laplace transformation these equations reduce to:

$$\begin{aligned}\zeta(s\langle\tilde{z}_n\rangle - z_n(t=0)) &= \frac{k_{\rm B}T}{b^2}\,\frac{\partial^2\langle\tilde{z}_n\rangle}{\partial n^2} + k_{\rm B}T\left(\frac{\pi}{2Nb}\right)^2\langle\tilde{z}_n(t)\rangle\\ \frac{\partial\langle\tilde{z}_n\rangle}{\partial n}\Big|_{n=0} &= 0\ (t > 0)\ \text{at the cut end}\\ \frac{\partial\langle\tilde{z}_n\rangle}{\partial n}\Big|_{n=\bar{n}} &= \tau b^2 s^{-1}/k_{\rm B}T\ \text{at the outer end}\end{aligned} \qquad (29)$$

The differential equation is solved by

$$\begin{aligned}\langle\tilde{z}_n\rangle &= a_1(n)\cosh(\sqrt{f(s)}n) + a_2(n)\sinh(\sqrt{f(s)}n)\ \left(s > \left(\frac{\pi}{2N}\right)^2\frac{k_{\rm B}T}{\zeta b^2}\right)\\ \langle\tilde{z}_n\rangle &= a_1(n)\cos(\sqrt{f(s)}n) + a_2(n)\sin(\sqrt{f(s)}n)\ \left(s < \left(\frac{\pi}{2N}\right)^2\frac{k_{\rm B}T}{\zeta b^2}\right)\\ f(s) &= \left|\frac{b^2\zeta s}{k_{\rm B}T} - \left(\frac{\pi}{2N}\right)^2\right|\end{aligned} \qquad (30)$$

The functions $a_1(n)$ and $a_2(n)$ are obtained by the constant variation method and explicitly depend on the initial configuration $z_n(t = 0)$. We are interested here in the case where the initial configuration corresponds to the minimal path, which is the stationary solution of the Rouse equation, eq 6, with the boundary conditions in eq 28:

$$z_n(t=0) = \frac{2N\tau b^2}{\pi k_B T} \frac{\sin\left(\frac{\pi n}{2N}\right)}{\cos\left(\frac{\pi \bar{n}}{2N}\right)} \qquad (31)$$

We only consider the high-frequency solution $s > 1/T_R$, and we restrict ourselves to that case in the following. The position z_0 of the cut end point varies then as

$$\langle \tilde{z}_0 \rangle(s) = \frac{1}{s\sqrt{f(s)}} \frac{b^2\tau}{k_B T} \frac{\coth(\sqrt{f(s)}\bar{n})}{\cos\frac{\bar{n}\pi}{2N}} \qquad (32)$$

In the short time expansion, at times shorter than the Rouse time of a chain section of length $\bar{n}$, the coth in eq 32 becomes unity. The resultant Laplace transform is readily inverted to yield eq 8 where $\cos(\bar{n}\pi/2N)$ is eliminated in favor of τ_S.

In the case of a sticker in a parabolic potential, considered in Section 3, the average Rouse equation and the boundary conditions in eq 29 are

$$\zeta(s\langle \tilde{z}_n \rangle - z_n(t=0)) = \frac{k_B T}{b^2} \frac{\partial^2 \langle \tilde{z}_n \rangle}{\partial n^2}$$

$$\zeta'(s\langle \tilde{z}_0 \rangle - z_0(t=0)) = \frac{k_B T}{b^2} \frac{\partial \langle \tilde{z}_n \rangle}{\partial n}\Big|_{n=0} - k\langle \tilde{z}_0 \rangle \qquad \text{(sticker end)}$$

$$\langle \tilde{z}_N \rangle = z_b/s \ \text{(outer end)} \qquad (33)$$

where the initial configuration is: $z_n(t = 0) = z_b n/N$. The Rouse equation is solved using the variation of the constant method to obtain $\langle z_0 \rangle(s)$ as given by eq 15.

Appendix B. Calculation of the Fluctuations

The calculation is performed for the sticker in the parabolic potential $U = kz^2/2$, the chain end being held fixed at z_b. The Rouse equation with its boundary conditions is written for $\delta z_n = z_n - \langle z_n \rangle$:

$$\zeta \frac{\partial \delta z_n}{\partial t} = \frac{k_B T}{b^2} \frac{\partial^2 \delta z_n}{\partial n^2} + f_n$$

$$\delta z_N = 0$$

$$0 = -\zeta' \frac{\partial \delta z_0(t)}{\partial t} + \frac{k_B T}{b^2} \frac{\partial \delta z_n(t)}{\partial n}\Big|_{n=0} - k\delta z_0(t) \qquad (34)$$

The corresponding eigenmodes read

$$\psi_p(n) = \sin(k_p n) - \tan(k_p N)\cos(k_p n) \propto \sin k_p(N-n) \qquad (35)$$

with the mode selection rule

$$k_p = \left(\frac{\zeta'}{\zeta} k_p^{\ 2} - \frac{b^2 k}{k_B T}\right) \tan(k_p N) \qquad (36)$$

and the dispersion law

$$k_p^{\ 2} = \frac{b^2 \zeta}{k_B T \tau_p} \qquad (37)$$

where τ_p is the decay time of the p-mode. It is convenient to define a scalar product for which the eigenfunctions are orthogonal:

$$\langle \psi | \varphi \rangle = \int_0^N \mathrm{d}n\ \psi(n)\varphi(n) + \frac{\zeta'}{\zeta}\psi\varphi(0) \qquad (38)$$

The last term on the right-hand side stems from the special status of monomer 0; it can be understood by noting that the integral in the scalar product should run over the friction $\zeta + \zeta'\delta(n)$ (and not over the contour length), accounting for the friction discontinuity at $n = 0$.

The Rouse series is now obtained by the standard projection method[30] using the eigenmodes eq 35 and the scalar product eq 38:

$$\langle \delta z_n^2 \rangle = b^2 \sum_p \frac{\psi_p^2(n)}{k_p^2 \langle \psi_p | \psi_p \rangle}(1 - \exp(-2t/\tau_p)) \qquad (39)$$

The fluctuations of the position of the cut monomer $n = 0$ are given by

$$\langle \delta z_0^{\ 2} \rangle = \frac{2b^2}{N} \sum_p f(k_p^{\ 2})(1 - \exp(-2t/\tau_p)$$

$$1/f(x) = \left(\frac{\zeta'}{\zeta}\right)^2 x^2 + x\left(1 + \frac{\zeta'}{\zeta N} - \frac{2\zeta' b^2 k}{\zeta k_B T}\right) + \frac{b^2 k}{k_B T}\left(\frac{b^2 k}{k_B T} + 1/N\right) \qquad (40)$$

The Laplace transform of the fluctuation reads

$$\langle \delta \tilde{z}_0^{\ 2} \rangle = 2\frac{b^2}{Ns} \sum_p \frac{k_p^{\ 2} f(k_p^{\ 2})}{k_p^{\ 2} + b^2 \zeta s/(2k_B T)} \qquad (41)$$

We now sum the p-series in eq 41. This is done by defining a function in the complex plane with residues corresponding to the terms of the series. Let $g(x)$ be defined as $g(x) = (\zeta' x^2/\zeta - b^2 k/(k_B T))\tan(xN) - x$ so that the roots of $g(x) = 0$ are the $\pm k_p$. In terms of the function $g(x)$, eq 41 reads

$$\langle \delta \tilde{z}_0^{\ 2} \rangle = 2\frac{b^2 \zeta}{\zeta' s} \sum_p \frac{k_p^{\ 2}}{g'(k_p)(k_p^{\ 2} + b^2 \zeta s/(2k_B T))\left(k_p^{\ 2} - \frac{b^2 k \zeta}{k_B T \zeta'}\right)} \qquad (42)$$

where $g'(x)$ is the derivative of $g(x)$. Let now $H(X)$ be the function in the complex plane defined through

$$H(X) = \frac{X^2}{g(X)\left(X^2 + \frac{b^2 \zeta s}{2k_B T}\right)\left(X^2 - \frac{b^2 k \zeta}{\zeta' k_B T}\right)} \qquad (43)$$

The function $H(X)$ has four poles arising from the last two factors in eq 43 and an infinite series of poles $\pm k_p$. The integral over a circle Γ centered at $X = 0$ of diverging radius vanishes: $\int_\Gamma \mathrm{d}X\ H(X) = 0$. The sum of the residues at all poles vanishes:

$$2\sum_p \frac{k_p^{\,2}}{g'(k_p)\left(k_p^{\,2}+\frac{b^2\zeta s}{2k_BT}\right)\left(k_p^{\,2}-\frac{b^2ks}{k_BT\zeta'}\right)} = \frac{\zeta'}{\zeta}\,\frac{1}{\left(\frac{b^2\zeta' s}{2k_BT}\right)+\frac{b^2k}{k_BT}+\sqrt{\frac{b^2\zeta s}{2k_BT}}\coth\left(\sqrt{\frac{b^2\zeta s}{2k_BT}}N\right)} \quad (44)$$

Inserting the value of the sum into eq 42, we obtain the Laplace transform of the fluctuations given in the main text under eq 15.

Appendix C. First Passage Probability Starting from a Thermalized Distribution

We propose an alternative to eq 17 in the case where the sticker does not start at the bottom of the potential but is initially distributed following Boltzmann's law $P(z,0) = P_{eq}(z)$. At $t = 0$, a sink is opened at $z = L$ with an annihilation frequency $r(z) = Q\delta(z - L)$ at positive times. The probability $P(z,t)$ to find the sticker at location z at time t obeys

$$P(z,t) = P_{eq}(z) - \int_{-\infty}^{+\infty} dz' \int_0^t dt'\, r(z')P(z',t')G(z,z'|t-t') \quad (45)$$

The annihilation process reduces the probability with respect to the initial distribution by the contribution of the paths where annihilation takes place. In the limit $Q \to \infty$ the first passage probability is $P_f(t) = QP(L,t)$:

$$P_{eq}(L) = \int_0^t dt'\, P_f(t')G(L,L,t-t') \quad (46)$$

This is solved in Laplace space by

$$\tilde{P}_f(L,s) = \frac{P_{eq}(L)}{s\tilde{G}(L,L|s)} \quad (47)$$

Expanding $\tilde{P}_f(s)$ at low s we obtain the mean first passage time:

$$T_f = \int_0^\infty \frac{dt\,(G(L,L,t) - P_{eq}(L))}{P_{eq}(L)} \quad (48)$$

which is the expression obtained from eq 18 in the high activation energy limit and used in the main text.

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