Polymer Brushes as Pressure-Sensitive Automated Microvalves

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ABSTRACT: We describe theoretically the flow of a good solvent through two closely spaced polymer brushes. The brushes expand in response to the shear flow and decrease the cross-sectional area for flow. As such, this assembly of polymer chains acts as both sensor and valve for microflow control and bypasses the need to construct an external feedback mechanism. The discharge through the brush-linked conduit is a nonlinear function of pressure, enabling different modes of valve operation. For brushes which extend moderately into the interslit region, the valve assembly maintains constant discharge over a wide range of pressure. For brushes which extend far into the interslit region, the valve assembly cuts off flow above a critical pressure, limiting the maximum discharge.

I. Introduction

The physical properties of polymer brushes[1,2] are important in the modification of surfaces and the stabilization of colloidal properties. A polymer brush consists of a large number of polymers end-grafted onto a planar surface. The polymers are grafted so densely that they overlap strongly and are forced to stretch away from the surface, forming an elastic layer. Recent experiment and theory focus upon the response of such a brush to an applied tangential surface force. Klein *et al.* demonstrated that a pair of opposing brushes, slid past one another in the presence of a good solvent, experiences a repulsive normal force.[3-7] This repulsion between sheared brush planes has been interpreted as a result of brush swelling under shear. In poor solvents, a sheared brush is predicted to shrink.[8]

Here we study the response of two opposing brushes, in good solvent, to an applied pressure drop (Figure 1). The pressure differential results in laminar flow which imposes a shear stress on the brush, causing brush expansion. This brush swelling reduces the cross-sectional area and solvent flow and thereby readjusts the prevailing shear stress. Both the tangential surface force and the brush swelling are determined self-consistently, resulting in a nonlinear pressure-discharge relation. The difference between this and the earlier studies is clear. In ref 3 a tangential surface force is applied and brush swelling is the result. In this work, a pressure drop is applied and both the prevailing shear force and the brush swelling respond in a way that depends upon the brush and channel characteristics.

It is convenient to describe this fundamental problem in terms of related applications. Experimental evidence for nonlinear pressure-discharge relations exists in the ultracentrifugation literature, where membranes are "fouled" by adsorbed proteins.[9-12] There are several theories which explain the nonlinear behavior in terms of protein adsorption onto the exterior surface of the membrane and not within the internal pores. In contrast, the description presented here describes the nonlinear pressure-discharge relation as a result of well-defined adsorption upon the internal pore surfaces. Rather than considering the disadvantageous process of pore fouling, we can consider the advantageous control of flow through these pores. The adsorbed polymer brush senses the shear force, responds by swelling, and thereby readjusts the shear, much like a series of sensors and valves used to control flow. Consequently, we can describe the system as a "brush-valve" whose pressure-sensitive response is the fundamental problem of interest.

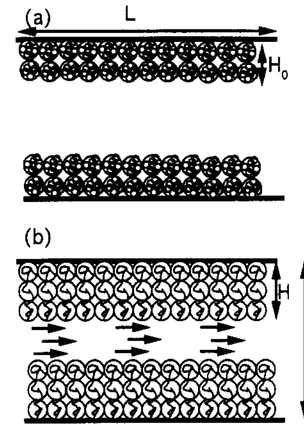

Figure 1. (a) Valve in the slit geometry. The polymer brushes, each of height H_0, are grafted to the top and bottom of a slit of length L, thickness W, and width $Z \gg W$ normal to the page. (b) When a fluid flows through the slit the brushes swell (if the solvent is good) to a height $H > H_0$. The flow only penetrates the brushes weakly, so the hydrodynamic thickness of the slit becomes smaller under flow. The brush swelling produces a closing of the slit and a dramatic reduction in discharge.

The brush sense-and-respond function can be implemented as an unconventional microvalve. Microvalves have been successfully manufactured using "silicon" technology, i.e., by selectively etching a silicon wafer.[13-16] These silicon microvalves are essentially microscopic versions of macroscopic valves and have gaps of order 100 μm, i.e., about 10^4 times larger than the brush-valves discussed here. Polymer brushes are attractive alternative materials for two reasons. First, they are soft; i.e., their moduli[17] are small and they thus respond sensitively to pressure. Second, they can exhibit a negative Poisson ratio;[18] i.e., they expand under shear, providing the cutoff and constant discharge control described in this paper. The proposed brush-valves have five potential advantages over conventional valve technologies.

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(1) The polymer brush is both the sensor and the valve. The brush responds automatically to flow without any external feedback control.

(2) The valve operates in very narrow tubes of the order of hundreds to thousands of angstroms, where traditional valve technologies fail.

(3) The valve is easily fabricated through self-assembly of end-functionalized polymers or block copolymers. Polymers can be adsorbed onto internal surfaces of porous media with pore sizes of order 100–4000 Å[19] or by microphase separation of a block copolymer matrix.[20–23]

(4) The valves should be less expensive to manufacture than silicon microvalves.[13–16] Moreover, the microvalves can be utilized in parallel, as, for example, polymer brushes lining the pores of a microfiltration membrane.

(5) Through choice of polymer and solvent quality, the valve can be fabricated to either open at low pressure and close at high pressure or vice versa.

These microvalves should have a number of practical applications, particularly in filtration systems, ink-jet printing, controlled drug release, and systems of medical and biological importance. In particular, the fact that the valve can limit the discharge to some maximum value or can set the discharge to some steady value might well prove useful in drug release systems. The reader should note that the brush-valve described in this paper is pressure sensitive and bidirectional; i.e., solvent can flow in either direction with equal ease.

Our description of brush-valves is limited to the case of good solvents where brush swelling, rather than brush compression, occurs with shear. We make a number of approximations in the discussion; these are necessary in part because the detailed hydrodynamics of flow through brushes is not well understood. We use the simplest model of brush structure, that of Alexander and de Gennes,[24] which assumes a homogeneous brush with the ends of each grafted chain residing at the tip of the brush. The reader should keep in mind that most of the numerical factors in the analysis are not accurate but that our study should nevertheless provide a qualitative description of brush-valve operation. The paper is arranged as follows. In section 2, the Barrat description of brush swelling under shear is reviewed. Although we use the Barrat picture throughout, the general idea that brushes can act as valves will be true no matter what particular detailed picture we use. In section 3, we describe an opposing pair of planar brushes under shear and derive a discharge versus pressure relation. In section 4 we discuss how such valves might be fabricated in practice. We conclude in section 5 with some limitations and possible extensions of the analysis.

II. Brush Swelling

In this section we discuss briefly the swelling under shear of a planar brush.[5,25] Each tethered chain in a brush can be pictured as a connected sequence of blobs.[26] The blobs are of radius $\xi = R_F^{5/2}/L^{3/2}$, where R_F is the Flory radius and L is the end-to-end distance of the chain. Within each blob the monomers are locally correlated as in a Flory excluded-volume chain. For distances larger than the blob size, the blobs act as hard spheres. The number of blobs per chain is given by $N_b = (L/R_F)^{5/2}$. The brush is an assembly of chains end-grafted onto the grafting plane with density $1/d^2$, where d is the distance between grafting points. The grafting density is assumed to be large; i.e., the chains overlap. Here we usually assume there are many blobs per chain, although experimentally N_b is often not much larger than unity.

When the brush assembly is sheared, the free chain ends are displaced distance X in the x direction, the chain is tilted, and the end-to-end distance, L, is increased. The number of blobs per chain, N_b, increases with L, further enhancing the excluded-volume interaction between blobs. As a consequence, the brush will swell: the height of the brush changes from H_0 to H. This is the mechanism for brush swelling proposed by Barrat.[5,25] To analyze the expected degree of swelling and chain tilt with applied shear, the free energy of a chain in the brush assembly can be expressed[5,25] as

$$F_{\text{chain}} = \frac{1}{2}kT\frac{L^2}{N_b\xi^2} + kT\xi^3N_b^{\,2}d^{-2}H^{-1} - F_{\parallel}X \qquad (1)$$

The first term represents the stretching penalty of a Gaussian chain of blobs[27] that opposes brush swelling and shear, the second term is the excluded-volume interactions among blobs that promote brush swelling, and the final term is the work performed by the shearing force $F_{\parallel}$ which tilts the chains, displacing the free chain end distance X in the x direction. In the absence of shear, $F_{\parallel} = 0$, $\xi = R_F^{5/2}L^{-3/2}$, $N_b = (L/R_F)^{5/2}$, and $H = L$, and the equilibrium brush height is found by minimizing (1) with respect to H:

$$H_0 = (2/5)^{1/3}d^{-2/3}R_F^{\,5/3} \qquad (2)$$

Under shear, the height of the brush, H, the end-to-end distance, L, and displacement X will depart from the zero-shear values of $H = H_0$, $L = H_0$, and $X = 0$. Noting that $L^2 = H^2 + X^2$ and introducing dimensionless variables $\epsilon \equiv X/H_0$ and $\Delta \equiv H/H_0$ that describe x displacement and swelling under shear, we can recast eq 1 in dimensionless form as

$$F(R_F/H_0)^{5/2}/kT = \frac{1}{2}(\Delta^2 + \epsilon^2)^{5/4} + \frac{5}{2}\Delta^{-1}(\Delta^2 + \epsilon^2)^{1/4} - f\epsilon \qquad (3)$$

Here $f \equiv F_{\parallel}\xi_0/kT$ is a dimensionless force acting on the brush tip, $\xi_0 = R_F^{5/2}/H_0^{3/2}$, and we have included the dependence of the blob size and blob number on L. The expected x displacement and swelling of a sheared brush are found by minimizing (3) with respect to ϵ and Δ, i.e., by writing $\partial F/\partial\epsilon = 0$ and $\partial F/\partial\Delta = 0$:

$$f = \frac{5}{4}\epsilon(\epsilon^2 + \Delta^2)^{1/4}(1 + \Delta^{-1}(\Delta^2 + \epsilon^2)^{-1}) \qquad (4)$$

and

$$\Delta^3 = 2 - \Delta^2(\Delta^2 + \epsilon^2)^{-1} \qquad (5)$$

These equations can be solved simultaneously, providing a relation between the x displacement and swelling,

$$\epsilon = \Delta\left(\frac{\Delta^3 - 1}{2 - \Delta^3}\right)^{1/2} \qquad (6)$$

and an explicit relation between shearing force and swelling,

$$f = \frac{5}{2}\Delta^{-3/2}(\Delta^3 - 1)^{1/2}(2 - \Delta^3)^{-3/4} \qquad (7)$$

or

$$\begin{aligned}\Delta &= 1 + 0.053f^2 \quad \text{for } f \ll 1\\ &= 1.26 - 0.45f^{-4/3} \quad \text{for } f \gg 1\end{aligned} \qquad (8)$$

Figure 2 displays the swelling as a function of the shearing force, (7). Notice that at small shearing force, the swelling

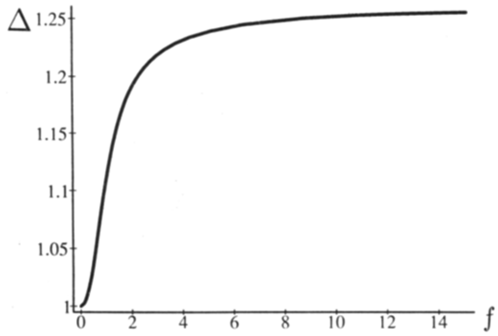

Figure 2. Dimensionless height of the brush Δ versus the dimensionless shear force per chain, f, according to the Barrat mechanism (eq 7). Initially the height grows as the square of the force. At very large forces the height grows to a maximum of about 125% of the unsheared height.

has the f^2 dependence expected from symmetry considerations and that at large shearing forces the swelling reaches a maximum of about 25%. This limit is evident from (5), where in the limit $\epsilon \to \infty$, $\Delta_{max} = 2^{1/3}$. Also of interest is the x displacement as a function of shearing force:

$$\begin{aligned} \epsilon &= 0.39f \qquad \text{for } f \ll 1 \\ &= 0.86f^{2/3} \qquad \text{for } f \gg 1 \end{aligned} \tag{9}$$

Note that for small forces this is just the expected displacement for an elastic layer with modulus kT/ξ_0^3.[17c] The blob size dependence on the swelling is

$$\xi/\xi_0 = (H_0/L)^{3/2} = (\Delta^2 + \epsilon^2)^{-3/4} = \Delta^{-3/2}(2 - \Delta^3)^{3/4} \tag{10}$$

An alternative "hydrodynamic" mechanism of shear swelling of brushes was recently proposed by Kumaran.[6] This provides swelling contributions that are of similar magnitude to Barrat's description. A more detailed description of the swelling would need to include these effects, but in general they will enhance the performance of the valves described here.

III. Valve Operation

For simplicity we study a channel formed from two parallel grafting planes of very large aspect ratio; i.e., the planar dimensions $L \times Z$ are large compared with the separation between planes, W. Flow is in the x direction and is caused by a pressure difference between $x = 0$ and $x = L$.[28] In the absence of grafted polymer the flow is simple laminar flow with average velocity[28]

$$\bar{v} = (P/L)W^2/(12\eta) \tag{11}$$

and discharge or volumetric flow rate[29]

$$Q = (P/L)ZW^3/(12\eta) \tag{12}$$

where η is the fluid viscosity and P is the pressure drop between $x = 0$ and $x = L$.

Consider the same grafting planes, separated by W and lined with polymer brushes of height H (Figure 1). To understand qualitatively the operation of the microwave assembly, the details of the brush structure are unimportant, but knowledge of the brush height as a function of the shear stress is critical. To a first approximation the fluid penetrates only weakly into the brushes and so can be described as laminar flow through a channel of effective height $W - 2H$. The discharge[28] is then

$$Q = (P/L)Z(W - 2H)^3/(12\eta) \tag{13}$$

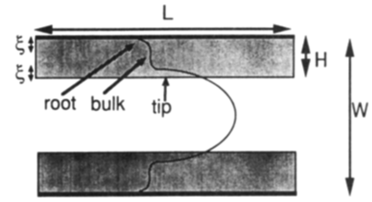

Figure 3. Approximate velocity profile in the slit, as used in the text. In the central gap where there is no polymer, we have laminar flow with a parabolic profile. For an Alexander–de Gennes brush this penetrates a distance ξ into the brush, i.e., into the tip region. In the bulk of the brush the flow is driven by the pressure gradient and has constant speed $v_p = \xi^2|\Delta P|/\eta$. Where the brush makes contact with the wall, the root, there is again a region of thickness ξ where the speed changes from v_p to 0.

The novel feature of this assembly is that H is a function of the pressure drop, P. This is particularly important since the discharge depends on the third power of $W - 2H$. Even a weak dependence of H on P provides a strong P dependence on the discharge, Q. Both theory[5,6] and experiment[3] indicate that H *increases* with increasing shear stress if the fluid is a *good* solvent for the grafted chains. As a result, the cross-sectional area of the brush-lined slit diminishes with pressure. The discharge through the brush-lined channel is then a nonlinear function of P. Several scenarios are possible, depending on the brush response to swelling. In general, we expect $Q \propto P^\alpha$, where $\alpha < 1$. The most desirable value of α depends on the application. If the valve is to maintain a constant discharge, then $\alpha = 0$ is needed; if the valve should close above a certain pressure, then $\alpha < 0$.

A dimensionless form of (13) is convenient:

$$q = p(1 - \beta\Delta)^3 \tag{14}$$

where $q \equiv 6Q\eta\xi_0^3/(kTW^2Z)$, $p \equiv (^1/_2)WP'\xi_0^3/kT$, where $P' \equiv -(\mathrm{d}P/\mathrm{d}x)$, and $\beta \equiv 2H_0/W$ is fraction of the gap taken up by the polymer brush in the absence of shear. Equation 14 contains the pressure-discharge relation but is not yet complete since the dependence of Δ on p is unknown. Our aim here is to find $\Delta(p)$. Our approach is to calculate the solvent flow through the entire conduit, i.e., through both brushes and the gap. This allows us to calculate the discharge through the conduit, to calculate the force on the brush, and to construct the relation $\Delta(p)$.

In the brush-free gap of size $W - 2H$, the flow is laminar[28]

$$\eta\frac{\mathrm{d}^2 v}{\mathrm{d}y^2} = -P' \tag{15}$$

where $P' \equiv -(\mathrm{d}P/\mathrm{d}x)$ is independent of x. Flow penetration through the brushes can be modeled as flow through porouos media, using the Brinkman equation[30] with the characteristic distance of the porous media being the blob size of the tethered chains:

$$\eta\frac{\mathrm{d}^2 v}{\mathrm{d}y^2} = -P' + \eta\xi^2 v \tag{16}$$

Here v is the velocity in the x direction and ξ is the blob size in the brush. Equations 15 and 16 can be solved exactly, subject to no-slip condition at the grafting planes, $v(0) = v(W) = 0$, and continuity of v and $\mathrm{d}v/\mathrm{d}y$ across the interfaces between brush and gap. However, the exact solutions of (15) and (16) are lengthy. We use a simpler approach. The flow penetrating the brush can be approximated by dividing the brush into three regions: tip, bulk, and root (Figure 3). At the root of the grafted chains, i.e., at the grafting plane, there is a region of thickness ξ

where the velocity increases from 0 (the no-slip condition) to v_p, the velocity within the bulk of the brush. The bulk of the brush acts as a porous medium of thickness $H - 2\xi$ with plug flow and, from (16), the velocity is $v_p = P'\xi^2/\eta$. At the tip of the brush, over a distance ξ the velocity varies from its value at the edge of the gap, found from (15), to v_p. Adding the discharge contributions from the gap + brush tip, the bulk brush, and the root regions yields

$$Q = Z\frac{P'}{\eta}\left[\frac{1}{12}(W - 2H + 2\xi)^3 + 2\xi^2(H - 2\xi) + \xi^3\right] \quad (17)$$

In the limit where $H \gg \xi$ and $W - 2H \gg \xi$ the discharge can be written as $Q = Q_g + Q_l$ where

$$Q_g = \frac{P}{L}\frac{Z}{12\eta}(W - 2H)^3 \quad (18)$$

is the discharge through the gap and Q_l is the "leakage discharge" penetrating the brush, given by $Q_l = {}^1/_2 ZP'\eta^{-1}\xi(W - 2H)^2$. Notice that the leakage discharge becomes significant only when $W - 2H \approx \xi$, i.e., when the brush-free gap is of the order of a blob size and the whole channel is blocked by polymer. Once this occurs, the channel acts as a porous medium. In the cases studied here, the gap is larger than the blob size, penetration of flow in the brush can be ignored, and the discharge is given by (13).

To determine the relation between brush height, H, and pressure gradient, P', we calculate the shear force acting on a single chain. In eq 1, the shearing force, $F_\parallel$, is assumed to act only at the tips of the tethered chains; however, there will be a force in the direction of flow throughout the brush due to flow penetration. The most recent experiments suggest that this penetration is very small.[4] An exact treatment of the shearing force would require an explicit expression for $F_x(z)$ over the range $0 < z < H$. This in turn would imply that the brush is inhomogeneous, with a blob size which varies with height. For simplicity, and in the spirit of the Alexander–de Gennes model, the total force acting on the tethered chain is assumed to be totally localized at the tip. This total force can be estimated by considering once again the three regions of the brush: tip, bulk, and root. In the region of thickness ξ near the chain roots, the flow velocity changes from 0 to v_p, the stress is $\sigma \equiv \eta|dv/dy| \equiv P'\xi$, and the force on each chain in the region $0 < z < \xi$ is thus $\sigma\xi^2 = P'\xi^3$. In the central region of the brush, of thickness $H - 2\xi$, a pressure gradient P' results in the force $\xi^2(H - 2\xi)P'$ acting on the chain within $\xi < z < H - \xi$. Finally, in the tip region of thickness ξ the velocity gradients are important and the force is $\xi^2\sigma = \xi^2\eta|dv/dy| = {}^1/_2\xi^2(W - 2H)P'$. The total shear force on the brush is the sum of the shear forces acting upon the tip, bulk, and root of the brush assembly:

$$F_\parallel = \xi^2 P'\left[\frac{1}{2}W - \xi\right] \approx (1/2)WP'\xi^2 \quad (19)$$

Note that for narrow gaps, where $W - 2H \approx H$, a significant fraction of the shear force arises from the bulk of the brush and the shearing work term in (1) is more appropriately expressed as an integral.

The blob size decreases with shear-induced swelling and extension and, from eq 19, the shearing force will also diminish with swelling. Using eq 10 and the dimensionless pressure $p \equiv {}^1/_2 WP'\xi_0^3/kT$, (19) can be written as

$$f = F_\parallel\xi_0/kT = \frac{1}{2}WP'\xi_0\xi^2/(kT) = p(\xi/\xi_0)^2 = p\left(\frac{2 - \Delta^3}{\Delta^2}\right)^{3/2} \quad (20)$$

Note that p is also the dimensionless force acting on a chain with blobs of size ξ_0 and that eq 20 demonstrates explicity that the shearing force on the chain is $((2 - \Delta^3)/\Delta^2)^{3/2}$ times smaller than it would be if the blob size remained at ξ_0. For small degrees of swelling $\Delta \approx 1$ this effect is negligible. However, when $\Delta \approx 2^{1/3}$ the force is much reduced. This effect is partly responsible for the discharge-pressure relation of the proposed brush-valve.

A relation between the dimensionless pressure, p, and swelling, Δ, is constructed from the thermodynamic $f - \Delta$ relation given in eq 7 and the mechanical f–Δ relation of eq 20. It is

$$p = \frac{5}{2}\Delta^{3/2}(\Delta^3 - 1)^{1/2}(2 - \Delta^3)^{-9/4} \quad (21)$$

This together with relation 14

$$q = p(1 - \beta\Delta)^3 \quad (22)$$

provides the implicit relation between pressure and discharge for brush-valve of equilibrium brush height described by β. These two equations give the $q - p$ curve parametrically. To plot the $q(p)$ curve we merely fix β and vary Δ.

The $q(p)$ curves are plotted in Figure 4 for three characteristic regimes, depending upon the equilibrium height of the brush relative to the conduit spacing, i.e., β. For small brush heights, $\beta < \beta_1 \equiv 0.78$,[31] the dimensionless discharge increases monotonically with dimensionless pressure as would be expected in the absence of a brush. The flow differs from laminar flow in that there are two distinct regions of flow resistance: at small pressures the resistance is low but increases at some crossover point (Figure 4a). Within a small window of moderate brush heights, $\beta_1 < \beta < \beta_c \equiv 2^{-1/3} = 0.79$, the discharge increases rapidly with initial pressure, attains a maximum, and then exhibits a plateau region that persists over a wide range of pressure with only mildly increasing q (Figure 4b). The plateau region corresponds to a constant-flow valve where perturbations affect the discharge insignificantly. For larger brushes, $\beta > \beta_c$, the discharge increases with initial increase in pressure, reaches a maximum, and falls to zero discharge. The cutoff pressure, i.e., the pressure at which the discharge is zero, is found by setting $\Delta = \beta^{-1}$ in (22) and (21), giving

$$p_c = \frac{5}{2}\beta^{15/4}(1 - \beta^3)^{1/2}(2\beta^3 - 1)^{-9/4} \quad (23)$$

The ratio brush height to gap, β, is a design parameter which determines the cutoff pressure, p_c, in the range $\beta > 0.80$ (Figure 5).

The dimensionless pressure $p = ({}^1/_2)WP'\xi_0^3/kT$ is an important parameter in valve design. The term kT/ξ_0^3 is the osmotic pressure in the brush[26] and also the elastic modulus of the brush.[17] As the interesting valve behavior occurs for values of p on the order of 1 (Figure 4), the operating range of P' must be roughly $kT/(W\xi_0^3)$. In other words, the valve effects occur when the applied force per unit area of the brush equals the osmotic pressure. Loosely grafted brushes are "soft"; i.e., they have large blob sizes ξ_0, possess small moduli, and are sensitive to small fluctuations in pressure. In contrast, more densely grafted brushes have smaller blob sizes ξ_0 and larger elastic moduli, and consequently do not respond as dramatically to pressure fluctuations. The appropriate pressure gradient $P' = kT/(W\xi_0^3)$ is clearly very sensitive to the blob size ξ_0 and hence to the grafting density. To examine some numerical examples we take $W \sim \xi_0$, so $P' \approx kT/\xi_0^4$. For a weakly grafted brush $\xi_0 \approx 1000$ Å and $P' \approx 4 \times 10^7$ Pa/m $\approx 10^2$ atm/m. For a membrane of thickness 100 Å this corresponds to a pressure drop of 10^{-5} atm. However, for

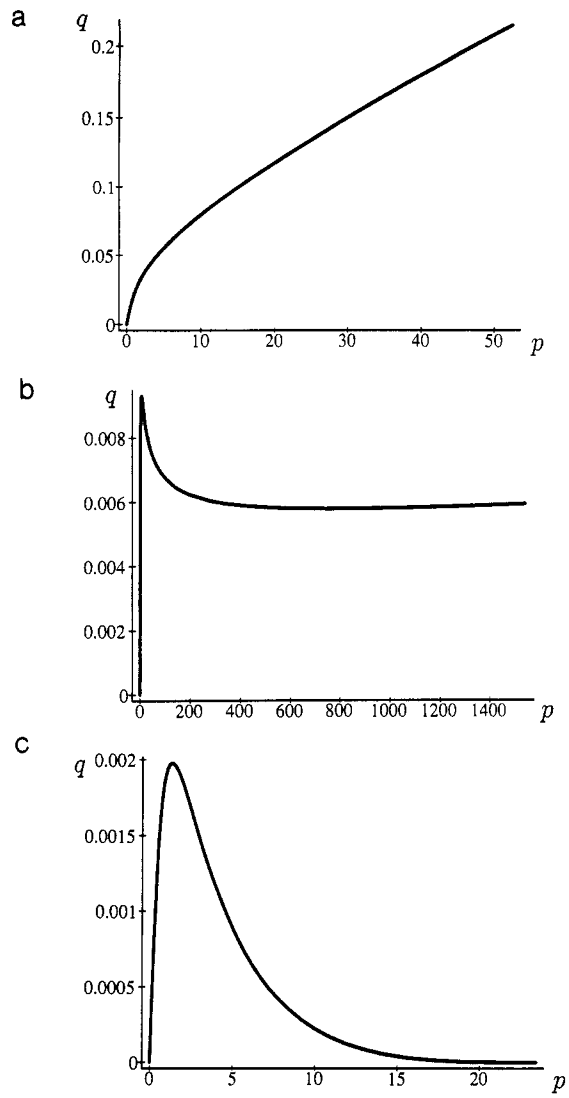

Figure 4. Dimensionless discharge q versus the dimensionless pressure p for various values of $\beta = 2H_0/W$, one for each regime. (a) $\beta = 0.7$. The gap is initially wide. At low pressures the height of the brush is not changed significantly by the flow. The discharge is thus proportional to the pressure. At high pressures the force on the brush is large and it expands to its maximum height of $2^{1/3}H_0$. However, there is still a large gap and the discharge is again proportional to the pressure. Intermediate to these two cases the brush expands. (b) $\beta = 0.79$. The gap is initially narrower than in (a). The dischage grows rapidly to a maximum, declines, and then levels off to a constant value. It is constant over a wide range of pressures. Eventually the discharge increases again with pressure but this occurs off the graph. For this value of β the brush grows in height, but as in (a) it never closes the channel completely. The slit acts as a "constant-discharge" valve. (c) $\beta = 0.85$. Initially there is a narrow gap. The brush thus expands to fill the gap and the flow is cutoff entirely at a critical pressure $p \approx 25$. The slit acts as a pressure-sensitive valve, only letting flows through which have a small pressure gradient. In doing so it also limits the discharge to a maximum value.

a more densely grafted brush with blob size $\xi_0 = 100$ Å and again with $L = 1000$ Å, the pressure drop is much larger, 0.1 atm.

IV. Valve Manufacture

There are several possible methods of fabricating the microvalves discussed above. In previous studies, polymer brushes have been constructed by adsorbing end-functionalized chains onto well-defined surfaces. Klein adsorbed polystyrene with zwitterionic end groups onto a pair of mica sheets separated 95–155 nm, in toluene, a good solvent.[3] For many practical applications the solvent

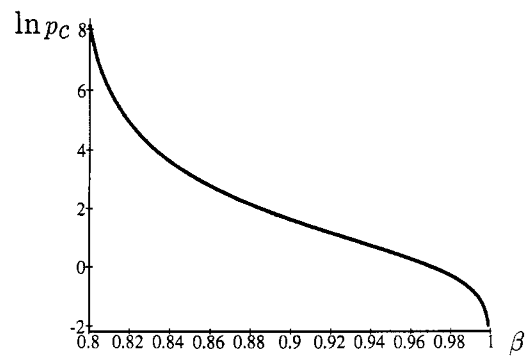

Figure 5. Natural logarithm of the dimensionless cutoff pressure $\ln(p_c)$ versus the gap parameter, β, for a valve operating in mode 3. For small initial gaps $\beta \approx 1$ the cutoff pressure is very small, but for gaps approaching the critical value, $\beta_c = 2^{-1/3}$, the critical pressure can become very large.

will be water and hence water-soluble polymers must be used. Auroy *et al.*[19] adsorbed hydroxyl-capped poly(dimethylsiloxane) onto a chromatographic silica support with well-defined pores of diameter 4000 Å in a variety of solvents. Repeating Auroy's fabrication using a medium with unidirectional pores, i.e., a membrane, would result in a parallel array of microvalves. Such an array would facilitate measurement of microvalve function. Poly(methyl methacrylate) chains have also been end-grafted directly onto membrane pores,[32] although no flow measurements for this system have yet been reported. From a practical point of view the reader might worry about chains being pulled off the surface by a flow. As discussed in refs 5 and 4, this appears to be unlikely for chains which have zwitterionic stickers.

Besides end-functionalized polymers, diblock copolymers will assemble into a brush under appropriate solvent conditions. In a solvent poor for the shorter block, the shorter block will adsorb to a sorption plane and the longer block for which the solvent is good will extend away from the plane, forming a brush assembly. Webber *et al.*[33] have adsorbed diblock copolymers onto pores but have used brush thicknesses which are much smaller than the pore radius. Finally, random copolymers having multiple functional or sorptive sites along the backbone may prove promising. Although the polymeric layer would be comprised of loops and trains rather than brush bristles, the excluded-volume effect should still swell the layer under shear. The procedure runs the hazard of blocking the pore if a significant number of chains bridge opposing surfaces.

Another possible fabrication technique relies on neither polymer adsorption nor the presence of a grafting technique but invokes phase separation to construct brush-lined conduits within a copolymer matrix. The technique uses ABA triblock copolymers which phase separate into glassy A regions and B regions on the order of 500 Å and form a mesogel.[20–23] The interface between A and B regions is similar to a grafting plane for loops formed of the B block. A few ABA chains bridge the soft B domains, interconnecting the domains for mechanical integrity of the copolymer matrix. A continuous B domain acts as a brush-lined conduit for which microvalve operation should hold. The size and shape of the conduits, i.e., the micromorphology, are determined by the size of the blocks and can be altered by mechanical stress. For example, if the sizes of the A and B blocks are equivalent, a lamellar micromorphology is expected and the self-organized mesogel corresponds to a parallel array of narrow slits. A brush adsorbed onto a circular channel, such as would normally occur in a membrane, is more "stiff" than a brush grafted with the same density onto a planar channel.

Consequently, the mesogel system provides a simple method for fabricating a parallel array of slits which may demonstrate a more dramatic pressure effect than brush-lined membranes.

V. Discussion

In this paper we have described the operation and fabrication of a pressure-sensitive switch or valve using polymer brushes. The microvalve control results from the swelling of the polymer brush with shear. Our discussion was limited to the Barrat swelling mechanism and is approximate. However, the qualitative conclusions we draw should be general. For brushes which fill the gap or conduit moderately, the brush pair acts as a constant-discharge microvalve. For brushes which nearly fill the gap, i.e., >80% of the distance between grafting planes, the brush pair behaves as a cutoff microvalve, limiting the maximum discharge. Loosely grafted or "soft" brushes respond more dramatically to pressure than densely grafted brushes and are expected to provide the most sensitive valves. In the limit of very dilute grafted chains, below overlap, the flow distortion is described in a recent paper of Brochard-Wyart.[34]

There are a number of approximations constructed in this first description of brush microvalves. Among these is the use of the Alexander–de Gennes "step function" for the chain end distribution. This ansatz is appealing because it simplifies all brush calculations. However, it is not exact. In particular, for a brush in a weak shear flow the hydrodynamic penetration length has been predicted to be $(H_0\xi_0)^{1/2}$ rather than ξ_0.[35] Although there are good theoretical grounds for believing in this enhanced penetration, it appears to be contradicted by the most recent experiments,[36] which show a very weak penetration. We thus believe that our approximation of a force acting on the brush tip and no flow into the brush is a reasonable one. Another limitation of the description arises from the blob assumption. The number of blobs per chain is given by $N_b = (L/R_F)^{5/2}$ and hence the number of monomers per blob is $n = N/N_b = N(R_F/L)^{5/2}(L/L_0)^{-5/2} = n_0(\Delta^2 + \epsilon^2)^{-5/4}$, where n_0 is the number of monomers per blob before shearing. As the brush is sheared, n decreases steadily and at about $\Delta = 1.2$ we find $n = n_0/10$. If the number of monomers per blob is too small, the blobs cease to be meaningful entities and in particular cease to repel each other like hard spheres. In addition, we have assumed negligible "leakage discharge" through the brush itself. Flow penetration is always present, even when the gap is closed or filled with polymer brush. However, it is likely to be small, even when the gap is of the order of one blob size. This is essentially because the term $v\eta/\xi^2$ in (16) is an approximation to $\eta v/k$, where $k = \xi^2 f(\phi)$ and $f(\phi)$ is a function of the packing fraction of spheres or blobs ϕ.[30] In particular, for large packing fractions ϕ, $f(\phi)$ becomes much larger than unity. That this must be so is fairly clear. An empty capillary of radius ξ offers much less resistance to flow than a capillary full of blobs of radius ξ. Finally, in the experimental results[3,4] there exists a critical shear velocity below which no normal repulsive forces are measured in the surface force apparatus. Barrat[5] has interpreted this critical shear as the shear required to swell the brushes to contact. The reader should bear in mind that something more subtle than this may be occurring. Our pressure-discharge relation should remain qualitatively correct, whatever the reason for this critical velocity.

We have limited our discussion to the case of rectangular slits. In practice, roughly circular, brush-lined channels may be easier to fabricate. Circular channels have the advantage that the discharge scales as the fourth power of the radius, and hence any swelling has a larger effect than in the rectangular geometry. However, chain crowding near the center of the channel also increases the effective modulus at the brush tip, suggesting that the assembly is less sensitive to pressure.

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(29) Strictly speaking, the discharge is the mass flow per unit time. What we have here is the volume flow per unit time.[28]
(30) See, for instance, Chapter 6 and references therein of: Scheidegger, A. E. *The Physics of Flow through Porous Media*; University of Toronto Press: Toronto, 1960.
(31) β_1 is obtained as follows. In general, the q versus p plot has a maximum and a minimum. These are given by solutions of 0 = dq/dp, which implies $0 = dq/d\Delta = (dp/d\Delta)(1 - \beta\Delta) - 3\beta p$. This equation only has two real roots for $\beta > \beta_1$. For $\beta < \beta_1$ there are no real roots and the $q(p)$ relation is monotonic.
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