Measuring the Work of Adhesion between a Soft Confined Film and a Flexible Plate

Animangsu Ghatak,[†] L. Mahadevan,[‡] and Manoj K. Chaudhury*,[†]

Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

Received June 19, 2004. In Final Form: November 2, 2004

We present a theoretical and experimental study of a method for the determination of the adhesion strength between a thin elastomeric film bonded to a rigid substrate and a flexible plate in a geometry common in the peel test. In particular, we characterize the work of adhesion in terms of the length of an equilibrium crack, generated by a spacer of known thickness wedged between the flexible plate and adhesive film, and the elastic and geometric properties of the film and the plate. We treat both the limit of perfect bonding and that of perfect slippage at the interface of the adhesive film and the flexible plate. A series of experiments allow us to verify the theory quantitatively and thus validate our method, which ought to be of value in many technological situations.

Introduction

Adhesion in many situations involves a soft adhesive interacting with flexible adherents. Despite the generality of this system in both technology and nature, it is not yet clear how the dual effects of adhesive thickness and adherent flexibility can be used to obtain controlled adhesion between different objects. Conventional contact mechanics[1−3] experiments were designed for estimating the work of adhesion between two semi-infinite elastic or rigid members. Modifications of the now classical Johnson−Kendall−Roberts (JKR) theory to experiments involving an adhesive layer of finite thickness result in semiempirical expressions for the work of adhesion,[4,5] while probe tack experiments account for the effects of the finite thickness of the adhesive but not the flexibility of the contacting plate.[6,7] On the other hand, the classical peel or cantilever beam experiments[8,9] do mimic the adherence of a flexible backing to a thin layer of adhesive. However, since the adhesive and the flexible backing are typically subject to large deformations in the peel experiment, separating their respective contributions is challenging both experimentally and theoretically. In this paper, we redress this by focusing on the linear regime of the cantilever peel test and develop a systematic theoretical and experimental method that accounts for both material and geometrical parameters. This allows us to determine the strength of this soft joint by combining the simplicity of the peel geometry and the rigorous analysis of contact mechanics.

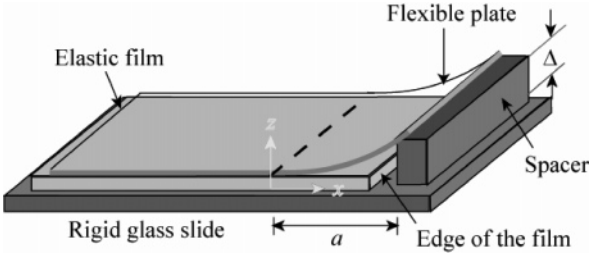

Figure 1. Schematic of a cantilever plate experiment in which a thin elastic film bonded to a rigid substrate is used as a model adhesive. A flexible silanized glass plate of bending rigidity D is peeled from the film in a displacement-controlled experiment by inserting a spacer of height Δ between the plate and the film. The distance a of the contact line (the dashed line) from the spacer is a measure of the adhesion strength between the two surfaces.

Theory

In a typical setup, shown in Figure 1, a thin elastic film of thickness h (40−450 μm) bonded to a rigid substrate is used as a model adhesive.[10] A flexible silanized glass coverslip of bending stiffness[12] D is peeled from the thin film in a displacement-controlled experiment by inserting a spacer of height Δ in the crack. The distance a between the spacer and the line of contact of the film and the plate is a measure of the adhesion strength of the interface.

To determine the work of adhesion, we must analyze the contact mechanics of this coupled elastic system. Assuming that the adhesive layer is incompressible, linearly elastic, and loaded in plane strain, the two-dimensional equations of elastic equilibrium may be written as

$$P_x = \mu(u_{xx} + u_{zz})$$
$$P_z = \mu(w_{xx} + w_{zz}) \qquad (1)$$

Here and elsewhere $a_b = \partial a/\partial b$. $P(x,z)$ is the pressure in

* To whom correspondence should be addressed. E-mail: mkc4@lehigh.edu.
† Lehigh University.
‡ Harvard University.

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(12) Flexural rigidity is defined as $D = \mu' t^3/3$ where t and μ' are the thickness and shear modulus of the flexible plate.

10.1021/la0484826 CCC: $30.25
Published on Web 00/00/0000 PAGE EST: 4.4

the elastic layer, $u(x,z)$ and $w(x,z)$ are the components of the displacement field in the x and z directions (Figure 1a), and μ is the shear modulus of the adhesive. Equations 1 must be supplemented by the incompressibility relation:

$$u_x + w_z = 0 \tag{2}$$

As shown in Figure 1, in the presence of a spacer of height Δ, a crack of length a opens up. For elastic films of sufficiently small thickness or for flexible plates of sufficiently large stiffness, the crack front or contact line does not remain straight but becomes wavy.[10] For simplicity, here we will only consider the case of a straight contact line. Assuming that we have perfect bonding at the interface of the adhesive film and the underlying rigid substrate, the boundary conditions at this interface are

$$u(x,0) = 0 \qquad w(x,0) = 0 \tag{3}$$

At the interface of the film and the flexible plate, the latter is in contact with the film only over part of the domain. Since the maximum slope of the flexible plate is less than 1°, we may use a linear theory for the deflection of the plate. In the region $0 < x < a$, with the origin corresponding to the contact line, there is no traction either on the plate or on the film so that the boundary conditions read

$$P = D\xi_{xxxx} = 0$$
$$\sigma_{zz}|_{z=h} = 0 \quad \text{and} \quad \sigma_{xz}|_{z=h} = 0 \tag{4}$$

Here σ_{ab} denote the components of the two-dimensional stress tensor (and not derivatives), and $\xi(x) = w(x,h)$ denotes the vertical deflection of the plate. In the region $x < 0$, continuity of the normal stress across the interface of the film and the contacting plate ($z = h$) yields

$$P = D\xi_{xxxx} \tag{5}$$

For the tangential traction, we consider the following generalized boundary condition:

$$\alpha\sigma_{xz}(x,h) + \frac{(1-\alpha)\mu}{h}u(x,h) = 0 \tag{6}$$

where α is a parameter characterizing the nature of the bonding at the interface of the film and the cover plate. $\alpha = 0$ corresponds to a perfect adhesion at the said interface (case I), while $\alpha = 1$ implies that $\sigma_{xz}(x,h) = 0$ and corresponds to the case of perfect slippage at the interface (case II). In general $\alpha \in [0,1]$.

For a thin film ($x \gg z$), we may use the lubrication approximation[13] so that the equations of equilibrium 1 simplify to

$$P_x = \mu u_{zz} \tag{7}$$

$$P_z = 0 \tag{8}$$

Physically, this simplification results from the dominant balance between shear stress and the horizontal pressure gradients in these thin layers. Integrating eqs 7 and 8 in the region $x < 0$ and using the boundary conditions 3 yields

$$u(x,z) = \frac{D}{2\mu}\xi_{xxxxx}(z^2 - chz) \tag{9}$$

Here, the constant $c = 1$ for the case of perfect adhesion (case I) and $c = 2$ for the case of perfect slippage (case II). Substituting this result into eq 2, integrating the equation across the thickness of the film, and linearizing the result for small deflections yields an equation for the vertical displacement of the interface of the elastomeric film in the region $x < 0$ where it is attached to the flexible plate:

$$\xi_{xxxxxx} - \frac{12\mu}{Dh^3(3c-2)}\xi = 0 \tag{10}$$

We require that the solution of eq 10 decay far to the left of the contact line so that

$$\xi|_{x\to-\infty} = 0 \qquad \xi_x|_{x\to-\infty} = 0 \qquad \xi_{xx}|_{x\to-\infty} = 0 \tag{11}$$

Continuity of the displacement, slope, bending moment, and vertical shear force at the contact line results in the following four conditions:

$$\xi|_{0-} = \xi|_{0+} \qquad \xi_x|_{0-} = \xi_x|_{0+}$$
$$\xi_{xx}|_{0-} = \xi_{xx}|_{0+} \qquad \xi_{xxx}|_{0-} = \xi_{xxx}|_{0+} \tag{12}$$

In the region $0 < x < a$, the deflection of the flexible plate must satisfy the equation $\xi_{xxxx} = 0$ since it is freely supported. At $x = a$, where the flexible plate is supported by a spacer of height Δ, the following two conditions are consistent with a hinged support:

$$\xi_{xx}|_{x=a} = 0 \qquad \xi|_{x=a} = \Delta \tag{13}$$

Finally, at the contact line we must use a condition that determines the nature of the stress in its immediate vicinity. The Barenblatt/Dugdale cohesive zone approach suggests that the pressure at the crack tip will be on the order of the van der Waals disjoining pressure, the magnitude of which is in the range of 1 GPa. For rubbery materials, the modulus is about 1 MPa so that one may expect severe crack blunting[14] leading to a typical stress comparable to the modulus. At the molecular level, the normal stress near the crack tip is a product of the force f supported by a single chain and its areal density Σ. At equilibrium, balancing the chemical potential of the bonded and the detached chains implies that the normal stress near the crack is[15]

$$\sigma_n = \frac{\Sigma_0\sqrt{2k_s\phi}}{1 + \exp\left(\frac{\epsilon - \phi}{k_BT}\right)} \tag{14}$$

where Σ_0 is the areal density of bonded and unbonded chains, ϵ is the energy of interaction between the chain and the substrate, k_s is the spring constant of the chain, k_B is Boltzmann's constant, and $\phi = f^2/2k_s$ is the elastic energy stored in the chain. It is easy to show that the normal stress σ_n at the crack tip goes through a maximum near the crack tip with its value being proportional to the modulus of the polymer. This situation is quite similar to

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that reported by Vorvolakos and Chaudhury,[16] who found that the maximum frictional stress for a weakly interacting rubber and a flat substrate (where ϕ depends on sliding velocity) is also directly proportional to the modulus of the former. However, for our purpose, we will ignore these molecular details and assume that the pressure becomes maximally tensile in the vicinity of the contact line $x = 0$ (up to a molecular Flory-like length scale), i.e.,

$$P_x|_{x=0} = 0 \tag{15}$$

Solving eq 10 subject to eqs 11−13 and 15 for the film displacements $u(x,z)$ and $w(x,z)$ in the adhered region $x < 0$ and the displacement of the flexible plate $\xi(x)$ in the free region $0 < x < a$ yields

$$u(x,z) = \frac{6z(z - ch)F'}{(3c - 2)kh^3}\phi_1(x)$$

$$w(x,z) = \frac{z^2(3ch - 2z)F'}{h^3(3c - 2)}\phi_2(x) \qquad x < 0$$

$$\xi(x) = F'(2(ak + 1) + (3ak + 2)kx + ak(kx)^2 - (kx)^3/3) \qquad 0 < x < a \tag{16}$$

where

$$\phi_1(x) = e^{kx/2}\left(ake^{kx/2} + \frac{3ak + 4}{\sqrt{3}}\sin(\sqrt{3}kx/2) - ak\cos(\sqrt{3}kx/2)\right)$$

$$\phi_2(x) = e^{kx/2}\left(ake^{kx/2} + \frac{3ak + 2}{\sqrt{3}}\sin(\sqrt{3}kx/2) + (ak + 2)\cos(\sqrt{3}kx/2)\right)$$

and

$$F' = 3\Delta/(6 + 12ak + 9(ak)^2 + 2(ak)^3)$$

$$k^{-1} = ((3c - 2)Dh^3/12\mu)^{1/6} \tag{17}$$

Here F' and k^{-1} are the two characteristic length scales in the problem: the first accounts for the response of the plate to the displacement Δ of its pivoted end, while the second length scale[17] measures the relative deformability of the plate and the film in terms of the size of the effective contact zone identified by Dillard. For an incompressible elastic film, the dependence of k^{-1} on various parameters is different from that for a compressible film as derived by Kaelble,[8] who ignored the hydrostatic stress state of the adhesive and derived the length scale $k^{-1} = (Dh/\mu)^{1/4}$. We note that for typical parameter values associated with thin films ($\mu \sim 10^6$ N/m^2, $h \sim 10^{-4}$ m and $D \sim 0.02$ Nm, $kh \sim 0.2$), $kh \sim (\mu h^3/D)^{1/6} < 1$ so that we can simplify the expressions above by neglecting terms such as $(kh)^2$ and higher order terms.

Work of Adhesion. Having determined the deformation field, we now proceed to determine the work of adhesion W. The total energy of the system includes the bending energy of the cover plate, the elastic energy in the film, and the interfacial energy of adhesion and may be written as

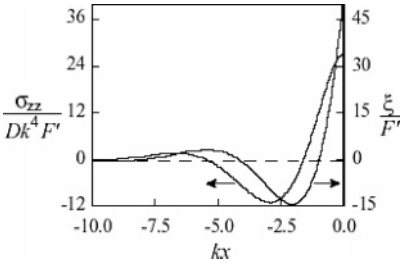

Figure 2. The dimensionless normal traction σ_{zz}/Dk^4F' and the dimensionless displacement $w(x,h) = \xi/F'$ at the interface ($z = h$) as a function of the dimensionless distance kx from the contact line show oscillatory behavior with an exponentially decaying amplitude. The curves correspond to $ak = 25$. Similar oscillatory displacement profiles with different decay lengths were first noted by Kaelble (ref 8) and observed in peel experiments using tracer particles (refs 20 and 21).

$$\prod(a) = \int_{-\infty}^{a} \frac{D}{2}\left(\frac{d^2\xi}{dx^2}\right)^2 dx + \int_{-\infty}^{0}\int_{0}^{h} \frac{\mu}{4}\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\right)^2 dz\, dx + Wa \tag{18}$$

where the deformation fields are as determined in the previous section. We note that when solutions 16 and 17 are substituted into eq 18, the result can be expressed in terms of a single parameter a, the crack length. Minimizing the total energy Π with respect to a, i.e., setting $\partial\Pi/\partial a = 0$, we get the work of adhesion W in terms of the crack length a. In the limit $kh < 1$ corresponding to the typical adherent geometry, this yields

$$W = \mathbf{G}_o g(ak) = \frac{9D\Delta^2}{2a^4}g(ak) \tag{19}$$

where the function $g(ak)$ for the perfectly bonded case (case I) and the free slippage case (case II) is

$$g(ak) = \frac{8(ak)^4(12 + 46(ak) + 72(ak)^2 + 56(ak)^3 + 21(ak)^4 + 3(ak)^5)}{3(6 + 12(ak) + 9(ak)^2 + 2(ak)^3)^3} \tag{20}$$

allowing W to be determined in terms of experimentally measurable quantities. When $ak \gg 1$, i.e., for an extremely pliable cover plate or for a rigid adhesive film, eq 19 simplifies even further and we recover the classical result of Obreimoff[18] for the peeling of a plate from a rigid substrate:

$$W = \mathbf{G}_o = \frac{9D\Delta^2}{2a^4} \tag{21}$$

Critical Normal Stress. The normal traction on the film surface is obtained from eq 16 since

$$\sigma_{zz}(x,h) = -D\xi_{xxxx} = -\frac{D\Delta k^4 e^{kx/2}}{6 + 12(ak) + 9(ak)^2 + 2(ak)^3}$$
$$(3ake^{kx/2} - 6(1 + ak)\cos(\sqrt{3}kx/2) + 2\sqrt{3}\sin(\sqrt{3}kx/2)) \tag{22}$$

In Figure 2 we plot the dimensionless normal traction σ_{zz}/Dk^4F' and the dimensionless vertical displacement ξ/F'

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as a function of the dimensionless distance kx from the contact line. We see that both σ_{zz} and ξ are oscillatory with exponentially decaying amplitudes away from the contact line.

At the contact line, the maximum tensile stress is

$$\sigma_{\max}|_{x=0} = \sigma_c = \frac{3D\Delta k^4(ak+2)}{6+12(ak)+9(ak)^2+2(ak)^3} \tag{23}$$

where σ_c defines the critical stress necessary to propagate a crack at the interface. In the limit $ak \gg 1$, $\sigma_c = 3D\Delta k^2/2a^2$ and $g(ak) = 1$. Thus, using eq 19, eq 23 can be rewritten in terms of the adhesion energy W as

$$\sigma_c = \frac{1}{kh}\sqrt{\frac{6W\mu}{(3c-2)h}} \tag{24}$$

Here $c = 1$ corresponds to the perfectly bonded case (case I) and $c = 2$ corresponds to the freely slipping case (case II), so that the critical failure stress σ_c for case I is found to be $2^{2/3} = 1.6$ times that for case II. It is useful to compare the above expression for the critical stress with that of a rigid cylindrical indenter of radius a being pulled off a layer of adhesive in contact with a rigid substrate, as derived by Yang et al.[19]

$$\sigma_c = \frac{a}{h}\sqrt{\frac{3W\mu}{2(3c-2)h}} \tag{25}$$

Here again, $c = 1,2$ refer to the cases of perfect bonding and free slippage as before. We note the similarity of eqs 24 and 25 up to the definition of a prefactor and the length scale k^{-1} which in our experiments with a flexible plate is equivalent to the radius of the indenter a. However, there is a qualitative difference in terms of how the critical stress varies with the thickness of the adhesive: $\sigma_c \sim 1/h^{3/2}$ for the rigid indenter, while $\sigma_c \sim 1/h$ for the flexible plate. In essence, the effect of finite thickness of the adhesive layer on the critical failure stress is somewhat more pronounced for a rigid indenter than for a flexible contacting plate.

Experimental Results and Discussion

Following the experimental protocol described in Materials and Methods, we measure the geometrical and material parameters for the peel test. For the purpose of comparison with theory, the expression for the work of adhesion given by eq 19 is rearranged to read

$$\frac{\Delta D^{1/2}k^2}{\gamma^{1/2}} = \left(\frac{W}{12\gamma}\right)^{1/2} f_1(ak) \tag{26}$$

where $f_1(ak) = (8(ak)^4/3g(ak))^{1/2}$ and $\gamma = 20$ mJ/m^2 is the surface energy of the poly(dimethylsiloxane) (PDMS) films. The crack length a for different spacer heights Δ, film thicknesses ($h = 50-450$ μm), and layer shear moduli ($\mu = 0.2-0.9$ MPa) and for cantilever plates of different flexural rigidities ($D = 0.02-0.84$ Nm) are scaled following eq 26 and plotted in Figure 3a which shows $\Delta D^{1/2}k^2/\gamma^{1/2}$ as a function of $f_1(ak)$. Here we have assumed that the bonding between the flexible cover plate and the adhesive film is perfect, corresponding to case I. We see that all data collapse on a single straight line going through the origin yielding the slope $(W/12\gamma)^{1/2} = 0.43$. Therefore $W = 44$ mJ/m^2, which compares well with the value of 42−44 mJ/m^2 obtained from JKR contact mechanics experiments

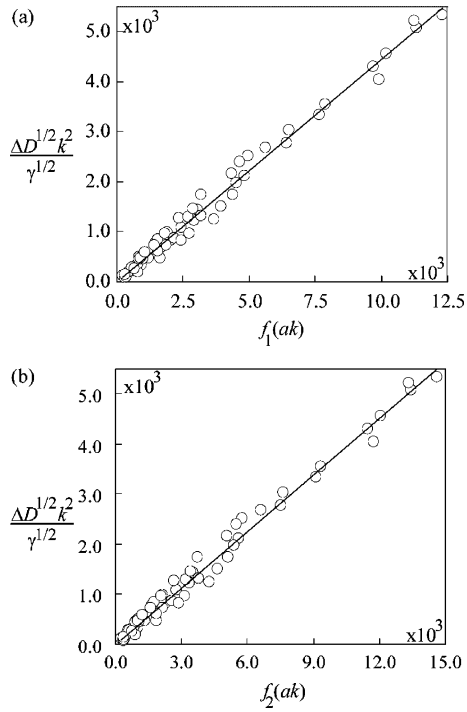

Figure 3. (a) The scaled displacement $\Delta D^{1/2}k^2/\gamma^{1/2}$ as a function of $f_1(ak)$ allows us to determine the work of adhesion W using eq 26. (b) The scaled displacement $\Delta D^{1/2}k^2/\gamma^{1/2}$ as a function of $f_2(ak)$ allows us to determine the constant C in eq 28, yielding a second comparison with theory.

of the same elastomeric networks[21] in contact with hexadecyltrichlorosilane-coated glass substrates.

For comparison with experiments, we also rewrite the expression for σ_c given in eq 24 as

$$\sigma_c = \frac{C}{kh}\sqrt{\frac{W\mu}{(3c-2)h}} \tag{27}$$

and determine the constant C using the experimental data. Substitution of this expression in eq 23 and subsequent rearrangement and normalization yields

$$\frac{\Delta D^{1/2}k^2}{\gamma^{1/2}} = C\left(\frac{W}{108\gamma}\right)^{1/2} f_2(ak) \tag{28}$$

where $f_2(ak) = (6 + 12ak + 9(ak)^2 + 2(ak)^3)/(ak + 2)$. In Figure 3b, we plot $\Delta D^{1/2}k^2/\gamma^{1/2}$ as a function of $f_2(ak)$ following eq 28 and see that the data nicely collapse on a single straight line passing through the origin with slope $C(W/108\gamma)^{1/2} = 0.36$, thus yielding $C = 1.78$. Expectedly, this value of C is somewhat lower than its theoretical asymptotic value of $6^{1/2}$ determined in eq 24.

When the experimental data are interpreted as corresponding to the case of free slippage between the adhesive film and the cover plate, i.e., case II, we find that $W = 46$ mJ/m^2 and $C = 1.8$. This relatively small difference between the two interpretations suggests that our experiments cannot really determine the nature of the contact between the elastomer and the plate which is likely to be neither perfectly bonded nor perfectly frictionless but subject to partial slippage. On the other hand, the critical failure stress σ_c estimated for different combinations of elastic films and the flexible cover plates varies from about 0.04 to 0.2 MPa, orders of magnitude smaller than that

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estimated from the van der Waals disjoining pressure (10^3 MPa assuming molecular contact over a range of a few angstroms) at the open surfaces of the crack. While it is tempting to infer that this rather large discrepancy is due to the roughness of the surfaces, very low values of σ_c measured even for atomically smooth surfaces suggest that roughness is not uniquely responsible for this discrepancy.

The theory and experiments presented here complement existing methods for measuring adhesion by accounting for the dual effects of the thickness of the adhesive film and the flexibility of the contacting plate, albeit in a geometry that involves small deformations. In contrast with the probe tack test involving the indentation of a cylindrical indenter of radius a into an adhesive layer, the peel test involves the appearance of a natural length scale $k^{-1} = (Dh^3/12\mu)^{1/6}$ which depends on the material and geometrical parameters in the problem. Tuning this length scale using these parameters thus allows us to probe a range of situations.

Materials and Methods

Vinyl end-capped poly(dimethylsiloxane) oligomers of molecular weights ranging from 2000 to 52000 received as a gift from Dow Corning Corp., Midland, MI, were used to form a thin adhesive layer. Hexadecyltrichlorosilane was bought from United Chemicals Technologies, Inc., Bristol, PA. The rigid substrates used in this experiment were Corning microslides with dimensions of 25 × 75 × 1 mm obtained from Fisher Scientific. The flexible plates were Corning cover plates also obtained from Fisher Scientific. The slides were oxygen plasma cleaned in a Harrick plasma cleaner (model PDC-23G, 100 W) before surface treatment. Two sets of filler gauges (spacers) of various thicknesses were used for making films of uniform thickness and were also used as the spacers.

Uniformly thin elastic films of PDMS were used as a model adhesive layer in our experiments. These cross-linked elastomers of shear moduli between 0.2 and 3.1 MPa were prepared by following the procedures described in refs 10, 11, and 16. The films remained strongly adhered to a rigid substrate. JKR[4] contact mechanics experiments of the networks indicated that they were purely elastic and exhibited no hysteresis. The work of adhesion for all these networks was estimated to be 40−42 mJ/m^2. Microscope coverslips coated with self-assembled monolayers of hexadecyltrichlorosilane (prepared following Ghatak et al.[10]) were used as flexible plates. The plate and the film were first rinsed thoroughly in deionized water to remove any static charge and blow-dried in nitrogen gas. The plate was then brought into partial contact with the adhesive layer with the help of a spacer that supported the plate at its free end and allowed to equilibrate till the crack length a did not change.

Acknowledgment. L.M. and M.K.C. acknowledge the financial support of the U.S. Office of Naval Research. A.G. and M.K.C. thank Dr. Jim Tonge of Dow Corning Corporation for providing the PDMS oligomers of different molecular weights.

LA0484826