Shear Rheology in a Confined Geometry: Polysiloxane Melts

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ABSTRACT: The dynamic mechanical shear response was measured of sharp fractions of molten siloxane oligomers, PDMS [poly(dimethylsiloxane)] and PPMS [poly(phenylmethylsiloxane)], confined between single crystals of muscovite mica, at film thicknesses <100 Å and a temperature of 23 °C. Five conclusions emerge. (1) A liquidlike mechanical response (in which the apparent dynamic viscosity was significantly enhanced over that of the bulk liquid) was clearly distinguished from a yield stress response (in which sliding over the experimental time scale occurred only after a critical yield stress was exceeded). These same features were observed previously for ultrathin films of smaller nonpolar molecules, and, despite quantitative differences in the present systems, the observation appears to be general. (2) The precise film thickness at the onset of the yield stress response, observed at film thicknesses <30–50 Å, did not depend on the molecular weight of the PDMS fractions but did depend markedly on details of the history of the experiment. (3) The yield stress increased with measurement time without a discernible change in separation. The times for the yield stress to reach a plateau increased with molecular weight and ranged from approximately 9 min (PDMS, M_n = 890) to approximately 400 min (PDMS, M_n = 6330) and approximately 650 min (PPMS, M_n = 2240). (4) Enhanced viscous response was observed at larger film thickness than for liquids of smaller molecules. The distance dependence of the apparent dynamic viscosity at 0.875 Hz was quantified for one sample (PDMS, M_n = 1670) by measuring the phase shift and amplitude attenuation in sinusoidal oscillation. The apparent dynamic viscosity appeared to diverge with diminishing film thickness. (5) After discussing how the act of shear may affect the structure of the liquid, we conclude that the yield stress rheological response may reflect a metastable, history-dependent state, in which relaxations of trapped chains have become slower than the experimental time scale of minutes to hours.

Introduction

The past several years have seen a great deal of theoretical, computational, and experimental effort devoted to investigations of the physics of molecular liquids and solutions confined to molecular dimensions. It is now generally accepted that the presence of a confining boundary induces local ordering of a fluid to an extent greater than is normally found in a bulk liquid radical distribution function. This local surface structure has been predicted for hard-sphere liquids by a large number of molecular dynamics simulations[1] and has been confirmed experimentally by surface force measurements of liquids trapped in a narrow slit between two confining boundaries.[2] In typical small-molecule systems, the molecular density profile displays a decaying oscillatory behavior as a function of distance from the wall, with alternating minima and maxima of a period of one molecular diameter. When the distance from the wall becomes great enough (usually 4–8 molecular diameters), the effects of the perturbing wall are completely screened and the molecular density becomes identical with the liquid bulk density.

Recently, computational and experimental efforts have begun to examine effects of similar small dimensions on polymer melt structure. Molecular dynamics simulations of chains near structureless solid surfaces show that, although there is a significant enhancement of segmental density very close to the surface, this enhancement is less than that found with atomic liquids.[3,4] Furthermore, the segmental density profile decays to the limit of the bulk fluid density within 2–3 segmental layers, more quickly than the profiles of small-molecule atomic fluids. These distinctions are due to the significant entropic penalty that a chain near the wall must pay to exist in a more highly related organized state; spherical particles, with no connectivity, are not affected by such configurational considerations.

These observations naturally lead to questions concerning the effect of such surface-induced structure on molecular dynamics. One might expect that the organization and confinement of molecules would lead to reorientation processes somewhat perturbed from the manner in which those processes occur in the bulk liquids. This might be manifested as an enhanced viscous dissipation of energy, and several techniques have been applied in attempts to measure this. Chan and Horn[5] used a modified surface force apparatus to show that the *drainage* (squeezing flow) behavior of relatively small molecules (*n*-tetradecane, *n*-hexadecane, and the cyclic tetramer of dimethylsiloxane) could be interpreted as if liquid molecules within 1–2 segmental layers of each surface did not exhibit fluidity over the experimental time scale. Horn and Israelachvili[6] used measurements of drainage rates to infer the viscosity of a poly(dimethylsiloxane) (PDMS) oil between crossed cylinders down to a thickness of closest approach of approximately 50 Å. They concluded that, although the dissipation was consistent with that predicted from the viscosity of the bulk oil, the data also suggested that a layer of molecules with thickness approximately 1 radius of gyration was immobilized near each of the experimental surfaces. Similar drainage measurements led to similar conclusions in studies of polybutadiene[7,8] and a recent reinvestigation of the PDMS system.[9]

In the above studies of melts of chain molecules,[5-9] as well as in a study of a melt of a perfluorinated polyether,[10] static force–distance profiles were also measured. Two conclusions emerged. First, it came to be recognized that

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the long-range forces that had been reported were not at equilibrium but reflected hydrodynamic forces, that is, slow drainage of the liquid from between the surfaces over the experimental time scale: the long-range repulsion was found to dissipate, the longer the experimental time scale.[9] At the same time, the force–distance profiles measured even over the longest time scales also showed persistent strongly repulsive "hard walls". This strong repulsion, which was observed at mica–mica separations of 30–50 Å, did not appear to depend on the experimental time scale. That it should likewise have a viscous origin is therefore not self-evident, and its physical origin remains mysterious. This provides one motive for the present experiments, which probe the *shear* response of polymer films at comparable separations.

Computer simulations of chain dynamics in confined media have recently begun to appear. Mansfield and Theodorou applied Monte Carlo techniques to study the effects of nearby surfaces on chains of a length of 20 segments.[3] Three cases were evaluated: "weak attraction" of chain segments to the surface (with segment–surface attractive potential less than a segment–segment attractive potential), "strong adsorption" (a large attractive segment–surface potential) with a high-energy barrier between adjacent adsorption sites, and strong adsorption with no energy barrier between adjacent adsorption sites. Results in all three cases indicated that chains with centers of mass within a distance of about 5 segmental units from the surface would have diffusion coefficients different from bulk chains. In the weak adsorption case, the lateral diffusivity was actually increased due to a low-density depletion layer formed near the surface. For the cases in which there was strong segmental adsorption, the lateral diffusivity was decreased by as much as 6 times; the effect of the adjacent site energy barrier was found to be small. Bitsanis and Hadziiouannou,[4] in molecular dynamics simulations, found that the influence of the surface on the diffusion coefficient was manifest only through the very locally enhanced density close to the attractive wall. This investigation concluded that chains without an appreciable number of segments within this interfacial layer of perturbed density would exhibit a diffusion coefficient identical with that in the bulk oligomer melt.

Our own experimental studies have concerned the shear of ultrathin liquid films confined between mica plates.[11,12] By use of oscillatory shear techniques developed in our laboratory, our studies of small-molecule liquids (primarily hexadecane and the cyclic tetramer of dimethylsiloxane) have suggested that liquid shear dynamics are severely retarded in films less than 50 Å thick.[11,12] Specifically, we have found for confined nonpolar liquids that the response to oscillatory shear excitation indicates dissipative processes, which, if interpreted as an apparent viscosity, are many orders of magnitude larger than those characteristics of the bulk liquids. At sufficiently small film thickness this dynamic shear behavior changes in dramatic fashion from one that is liquidlike to one characterized by the presence of a yield stress, i.e., suggestive of a solidlike state. A yield stress response has also been noted, by Israelachvili and co-workers,[13] in measurements made during shear at constant velocity. As will be discussed below, this yield stress shear response is found at separations comparable to those at which the strongly repulsive barrier is observed for forces in the normal direction.

We present here a report of extensions of our shear studies to polysiloxane oligomers comparable in dimension to the gap in which they are confined. This confinement leads to provocative and unusual dynamic shear response of the system. We shall postulate how the observed behavior may result from confinement of the chains and contrast the observations to those available from simulations.

Experimental Section

The experiments were conducted at the University of Illinois. The measurements of dynamic viscosity and yield stress employed an apparatus described in previous papers.[11,12] This apparatus is an extension of the well-known mica force balance apparatus.[14] Briefly, the liquid of interest was confined between two sheets of atomically smooth muscovite mica, the separation of the sheets being controlled and measured from <1000 Å down to molecular contact. The thin liquid film was forced in small-amplitude oscillatory shear by applying voltage to a driver piezoelectric element (spring constant 7000 $N \cdot m^{-1}$). A second, receiver, piezoelectric element was used to detect the resulting oscillatory motion. The forces typically applied in the experiments described below resulted in a shear amplitude of approximately 500 Å.

In some experiments, the sheets of muscovite mica were configured as smoothly curved cylinders oriented at right angles to one another, as in the traditional force balance apparatus.[14] As in our previous studies,[11,12] sheets of mica of identical thickness, silvered on the back sides with a highly reflective (60-nm) layer of silver, were attached to two cylindrical quartz lenses by using 2,4-diphenylcarbazide as glue.

Alternatively, when the normal pressure was sufficiently large, local flattening of the flexible mica sheets produced parallel plates at the apex of the crossed cylinders. The diameter of the parallel plates was on the order of 100 μm. Multiple-beam interferometry was used to measure the distance between the two surfaces, as well as either the local radii of curvature (if they were curved) or the area of contact (if they were flattened). This allows normalization of the measurements for the area of contact.

There is uncertainty regarding absolute calibration of the mica–mica thickness, and consequently of the film thickness, as we have discussed elsewhere.[25] The uncertainty refers to the effect of adsorbed gases during the experiment. If these dissolve into the liquid under study during the course of the experiment, then the convention used in some experiments[13] is appropriate to define zero as the mica–mica thickness measured at the end of the experiment after water has been added. In the present experiments, that assumption was not made and the zero was referred to the thickness measured before the experiment in dry nitrogen atmosphere. This zero is typically on the order of 5 Å larger than that measured in mica–mica contact in water. This uncertainty in the zero distance does not, of course, affect the relative film thickness but only its absolute magnitude.

The driving force function was varied depending on the type of behavior being investigated. When the film exhibited liquidlike behavior, the input function was sinusoidal and the dissipated energy per cycle was determined as an apparent dynamic viscosity from the amplitude attenuation and phase shift of the response signal. When the film exhibited yield stress behavior, the driving function used was a triangular ramp in shear force: this allows one to distinguish clearly the lateral shear force required to initiate shear motion. The temperature was 23 ± 1 °C. Pertinent experimental details are described in previous papers.[11,12] To anticipate later discussion, we note that although the changes in film thickness were well-defined during these experiments within the experimental resolution (±1–2 Å), strictly speaking the experiments were conducted at fixed net external normal pressure and not at fixed volume.

The three oligomers of methyl-capped poly(dimethylsiloxane) (PDMS) and one of poly(phenylmethylsiloxane) (PPMS) were kindly provided by Prof. S. J. Clarson of the University of Cincinnati and were used without further purification. The melting temperature of PDMS is T_m = −37 °C.[15] The glass transition temperature of PPMS is T_g = −20 °C.[16] Table I lists the number-average molecular weights used (M_n), the number-average degrees of polymerization (n_n), and the ratios of the weight-average molecular weight (M_w) to M_n.

Table I
Polymers Used in Shear Experiments, Number-Average Degrees of Polymerization (n_n), Number-Average Molecular Weights (M_n), and Approximate Times (Γ_{crit}) Required for the Critical Shear Stress To Reach a Plateau Level

polymer	n_n	M_n	M_w/M_n	Γ_{crit}, min
PDMS	12	890	1.01	9
PDMS	23	1670	1.01	
PDMS	85	6330	1.17	400
PPMS	16	2240	1.08	650

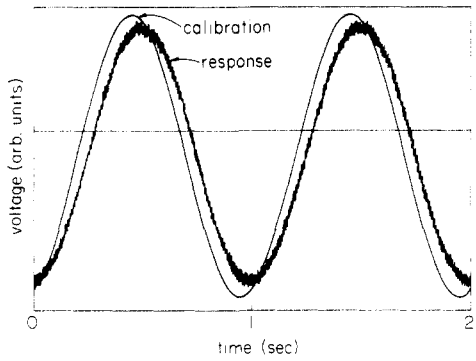

Figure 1. Experimental waveforms showing calibration and response waveforms. The apparent dynamic viscosity is calculated from the attenuation and phase shift of the response waveform with respect to the calibration.

Results and Discussion

Measurements of the dynamic response of confined chains suggest that the observed behavior may be divided into three categories. We shall refer to these as the viscous response, the solidlike response, and the transition from viscous to solidlike. Although the response observed is primarily determined by the thickness of the polymer film, it must also be emphasized that results are also sensitive to experimental detail, particularly to the rate at which the film is thinned. In repeated experiments on the same samples, the solidlike response we describe below was found to set in at thicknesses as large as 50 Å (if the mica–mica separation was reduced to this thickness over the course of less than 1 min) or as low as 30 Å (if the film was thinned to this thickness over the course of 0.25 h or more).

State otherwise, the states of the films were found to depend strongly upon the path taken to produce them. It appears that chain relaxation and reorganization in this confined geometry may be comparable to or slower than the experimental time scale of minutes to hours.[17]

Viscous Response. In repeated experiments, the viscous response was observed from the largest separations considered (tenths of microns) down to the range of onset of solidlike response, i.e., down to 30–50-Å film thickness. This loss of viscous response corresponds to a spacing between the solid surfaces of approximately 4–8 segment widths. Viscous energy dissipation increased markedly at separations below about 100 Å.

Figure 1 shows an example of the raw data. Traces are shown from an oscilloscope screen after averaging 100 oscillations. The waveform labeled "calibration" shows calibration of the mechanical response of the device itself when the mica surfaces were well-separated in nitrogen atmosphere. This waveform, whose ordinate is proportional to the displacement in response to sinusoidal excitation, depicts the sinusoidal voltage induced in the receiver piezoelectric bimorph. The "response" curve in Figure 1 shows the altered response at small film thickness. The voltage (proportional to displacement) was still sinusoidal with the same frequency, but it was attenuated in amplitude and it lagged in phase.

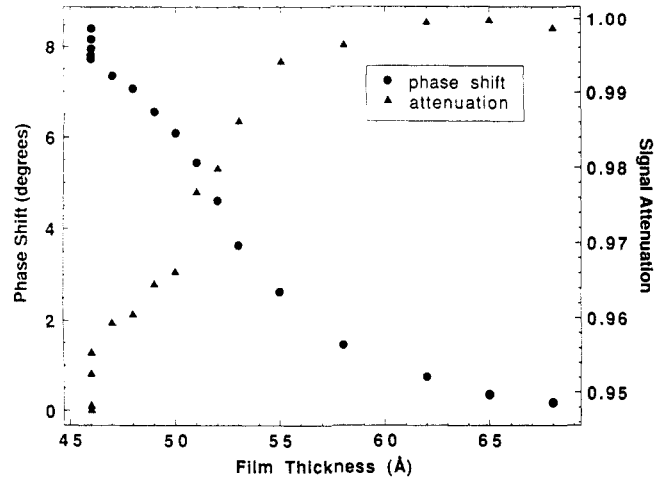

Figure 2. Phase shift and amplitude change plotted as a function of film thickness for PDMS (M_n = 1670). The frequency was 0.875 Hz.

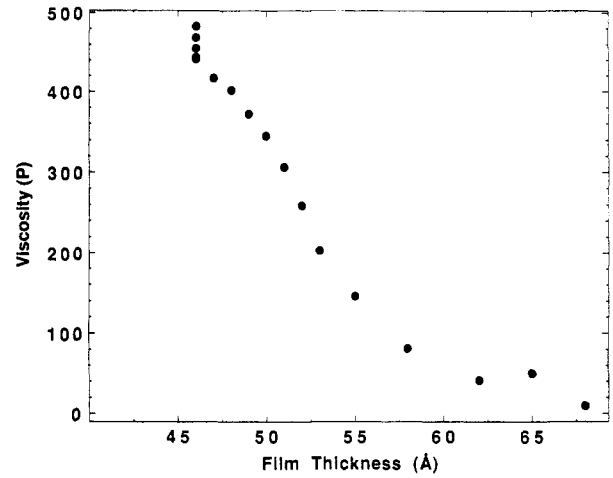

Figure 3. Apparent dynamic viscosity, calculated from the data in Figure 2 by the imposition of a hydrodynamic model for a sphere falling parallel to a wall,[19] plotted against film thickness.

Figure 2 illustrates the raw data taken as film thickness decreased as PDMS (M_n = 1670) drained from 70 to 46 Å, over the course of 10 min, as a result of thermal drift. The measurement frequency was 0.875 Hz, and the amplitude of oscillation was approximately 500 Å. As the film thickness decreased, the phase shift increased and the signal amplitude (proportional to the sliding distance traversed) decreased. If these data for the phase shift and amplitude attenuation are converted into apparent dynamic viscosity by the imposition of a hydrodynamic model appropriate for continuum fluids when a sphere moves parallel to a wall,[18,19] the apparent dynamic viscosity is found to rise monotonically with decreasing distance (Figure 3). At 46 ± (1–2) Å the phase shift and the apparent dynamic viscosity appear to diverge for the data shown in Figure 2 and 3. The bulk viscosity for PDMS of this chain length is far less—only approximately 0.25 P.[20]

It is true that the viscosity of a homogeneous liquid confined between two curved surfaces includes large contributions from fluid outside the region of least separation. We have discussed this in detail.[21] However, in the present situation the apparent dynamic viscosity changed rapidly with small changes in separation. This indicates that most of the signal came from a region of

enhanced dissipation near the point of least separation.

This enhanced dissipation suggests that relaxation processes of molecules within such films are severely restricted. In other words, long-range motions of molecules, when adsorbed within spaces of such radically small dimensions, are extremely difficult. In the bulk state, these oligomers are Newtonian liquids of low viscosity at the frequencies utilized.[20]

A comment should be made regarding the presentation of this data. Although the fluids in the experiment were surely inhomogeneous, it is for want of a better way to analyze the data that we have reported it, assuming well-known continuum relations,[19] as an apparent dynamic viscosity. Note that the assumption of a linear velocity profile between the solid surfaces and the location of the slip plane directly at the walls effectively supposes that the oligomer chains were not adsorbed onto the walls over the time scale of the oscillations. In fact the correct location of the "slip plane" becomes a relevant issue with experiments at such small separations, as discussed in the Introduction. However, we feel that it is pedagogically beneficial to present the data as an apparent dynamic viscosity, with the proviso that the reader be aware of how these values were deduced.

As we also found for hexadecane,[11] the apparent dynamic viscosity (the ratio of the maximum shear stress to maximum shear rate calculated assuming continuum relations) did not depend on the amplitude of the sinusoidal oscillations over the range of amplitudes investigated (500–2000 Å). In other words, the dissipative wall shear stress (the quantity determined experimentally) was directly proportional to the maximum velocity of motion as expected for a viscous response.

A natural question to ask is whether the shearing motion itself might have influenced the extent of viscous dissipation, perhaps by inducing orientation in the thin liquid film. For the data shown in Figures 2 and 3, data were taken in the course of repetitive oscillation; experiments were performed as the film drained from between the solid surfaces. Preliminary experiments in which shear motion was not performed during the course of drainage indicate that the measured dissipation, calculated as an apparent dynamic viscosity, is consistently and significantly higher (by approximately 2 times) if the shear is conducted concurrently with drainage. This suggests that the very act of performing the experiment may alter the organization of the confined fluid chains. This is a question to be pursued in future work.

Though further work is still needed to better quantify this finding of history-dependent measurements, it does have precedence in a diferent kind of surface forces experiment. Horn and co-workers[9] have noted that vibrations in their apparatus for measuring static force–distance profiles have led to deeper oscillatory minima measured in experiments with small molecules, presumably indicating a better developed density profile of the type discussed in the Introduction.

If one compares the range of film thickness of the data in Figures 2 and 3 to that in our previous measurements of the liquidlike response of hexadecane,[6] in which liquidlike response was observed at thickness <25 Å, we note that the liquidlike response was observed at significantly larger film thickness for the present siloxane oligomers. This raises questions of the possible role of segment–surface adsorption. The siloxane backbone is, of course, more polar than that of hexadecane and may be expected to adsorb more strongly to mica.

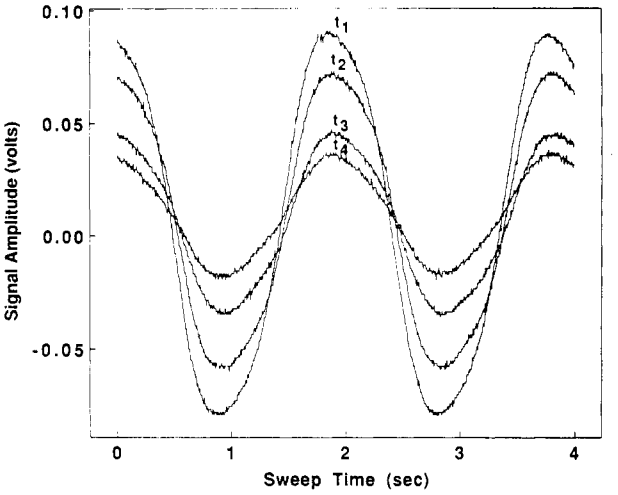

Figure 4. Transition from viscous to solidlike response, illustrated for PDMS (M_n = 6330). The film thickness was 20 ± (1–2) Å and the net normal pressure was 0.08 MPa. At time t_1 the signal amplitude was largest, indicating that the sliding surface was oscillating with the least viscous retardation. As time evolved from t_1 to t_4 (ca. 15 min), the signal amplitude became attenuated and the phase retardation grew. The signal eventually decayed to the signal characteristic of the compliance of the device.

Viscous to Solidlike Transition. The measured response to oscillatory shear stress changed dramatically, when the liquid film was sufficiently thin, from a viscous response to one in which a finite shear stress was required to initiate shear. The thickness at the transition (30–50 Å, as noted above) is comparable to the thickness of the strong repulsive "hard wall" barrier noted in previous force–distance measurements with other polymer oligomers: poly(dimethylsiloxane),[6,9] perfluorinated polyethers,[10] and polybutadiene.[7,8] Interpretation of those experiments was (as noted in the Introduction) complicated by lack of equilibration in measurements of the forces.[9] In the present experiments, we find solidlike response in *shear* at comparable separations. These shear findings suggest that the complete physical explanation of this viscous to solidlike transition remains to be found.

The pronounced change in behavior during the course of this transition is illustrated by the waveforms illustrated in Figure 4 for PDMS (M_n = 6330, film thickness 20 ± (1–2) Å, net normal pressure 0.08 MPa). Early in the transition (t_1) the system response was a distorted sine wave with large amplitude and phase shift. This distorted response became increasingly attenuated with time and eventually decayed to a heavily attenuated response, which reflected only compliance within the experimental apparatus (the mica and its underlying glue[11,12]). For the experiment illustrated in Figure 4, the elapsed time during the transition was 15 min. Note that adjustments in film thickness during the transition, although too small to measure in our experiments (less than 1–2 Å), could have been a significant fraction of the total thickness and could have produced significant changes in the average densities. The transition may in part reflect changes in the average density of the thin film, as we discuss below.

The transition was often, but not always, preceded by the draining of fluid from the gap and the concomitant thinning of the film by a separation corresponding to 1 or 2 segmental diameters. The absolute thickness at which the transition occurred was highly dependent on the rate of film thinning, however. In experiments with PDMS, the transition was measured to occur at thicknesses as small as 32 Å (approximately 4 segmental diameters) and as large as 49 Å (approximately 6 segmental diameters), with 36

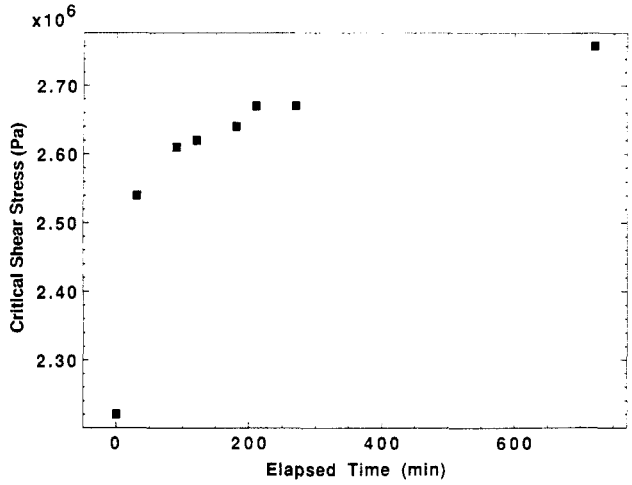

Figure 5. Critical shear stress plotted against elapsed time of the experiment for a PDMS sample (M_n = 6330) at film thickness 9 ± (1–2) Å and net normal pressure 2.8 MPa. The frequency of measurement was 1 Hz.

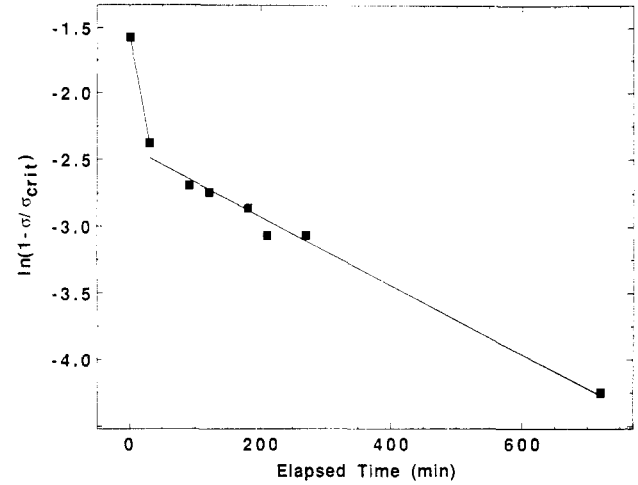

Figure 6. Same data as in Figure 5, replotted to show that the evolution of the critical shear stress may be described by two time constants. The quantity, $\sigma(t)$, is the critical shear stress. The quantity, σ_{inf}, is the plateau level of critical shear stress.

Å being the most commonly observed for the polymer fractions listed in Table I. Surprisingly, no systematic variation of the film thickness with the molecular weight of the polymers was noted.

When a liquid film was allowed to thin as slowly as experimentally practical (with drainage initiated by instabilities due to small ambient vibrations or to drift in the ambient temperature), the time elapsed during the transition from liquidlike to fully solidlike response did vary systematically with the molecular weight. The transition time ranged from approximately 30 s (M_n = 890) to approximately 15 min (M_n = 6330). This kinetics of was therefore slower, the larger the degree of polymerization. This suggests that the transition time may depend not only upon reorganization at the segmental level but also upon reorganization of the chains taken as a whole.

Solidlike Region. The observed change in response naturally raises question about the nature of molecular organization within these thin films. The sensitivity of the transition to experimental detail suggests that the chain molecules become trapped in nonequilibrium conformations. Perhaps, as we have discussed elsewhere,[12] the solidlike response may stem from a loss of free volume, in the sense of a progressive loss of orientational degrees of freedom to the point that slip between the solid surfaces can no longer be thermally activated but must be mechanically activated. This suggests the possibility that the solidlike response stems from a glasslike state, that of a metastable liquid with relaxations slower than the experimental time scale.

In order to penetrate into the solidlike region, it was necessary to impose external normal force. Generally, this force was sufficiently large to deform the mica sheets to the point that they flattened to form what appeared (in interferometry measurements) to be parallel plates. The area of these plates was measured from the flattened interference fringes in two orthogonal directions. Typically, the diameter of the spherical zone of contact was approximately 100 μm. This was measured continually throughout the experiments. The critical shear stress required to initiate shear was calculated as the critical shear force divided by the area of the mica plates.

Most provocatively, the critical shear stress required to initiate shear was found to increase with time. Figure 5 shows the time evolution of the critical shear stress for a PDMS fraction (M_n = 6330, net normal pressure 2.8 MPa). The measured film thickness remained constant at 9 Å; any associated changes in thickness were too small to detect (<1–2 Å), less than the thickness of a repeat segment, so it seems that the mass of the thin films did not change during annealing. In Figure 5, the critical shear stress increased by 25% in the course of the experiment, reaching an apparent plateau of 2.7 MPa after approximately 400 min.

Such an increase with time of the critical shear stress has been observed for every (nonpolar) fluid we have studied to date, including molecules that are not chainlike.[7] They have also been observed at larger film thicknesses; see Figures 7 and 8 for an example.

This observation suggests that some sort of reorganization of the film structure develops. The approximate times required for the critical shear stress to reach a plateau were found to depend strongly on molecular weight. As listed in Table I, the time to plateau, Γ_{crit}, ranged from approximately 9 min (M_n = 890) to approximately 400 min (M_n = 6330).

The fractional deviation of the actual critical shear stress, $\sigma(t)$, from its plateau value at long times, σ_{inf}, is plotted logarithmically against linear time in Figure 6 for the data shown in Figure 5. It is seen that a time constant empirically describes the long-time data well and that the short-time data (although much less complete) is also consistent with description according to a single time constant. This suggests the possible existence of two reorganizational processes. At relatively short times (less than a few minutes), when a relatively large degree of free volume may still be available, the time constant in Figure 6 is 37 min. At longer times, the time constant is 390 min. Further work is needed to elucidate the nature of the molecular organization that presumably develops during this time. In particular, as will be discussed below, we do not yet know from measurement if shear itself induces orientation within these films.

What is the molecular origin of the yield stress response? We have discussed above the possibility that the chains may become quenched into metastable glasslike states. On the basis of computer simulations, the possibility of crystallization has also been discussed.[22,23] This provided a motive to investigate the response of a glass-forming liquid, as we now describe.

Experiments with a Glass-Forming Liquid. Other experiments concerned a poly(phenylmethylsiloxane) (PPMS) fraction with M_n = 2240 as specified in Table I. Segments of PPMS are less symmetric than those of

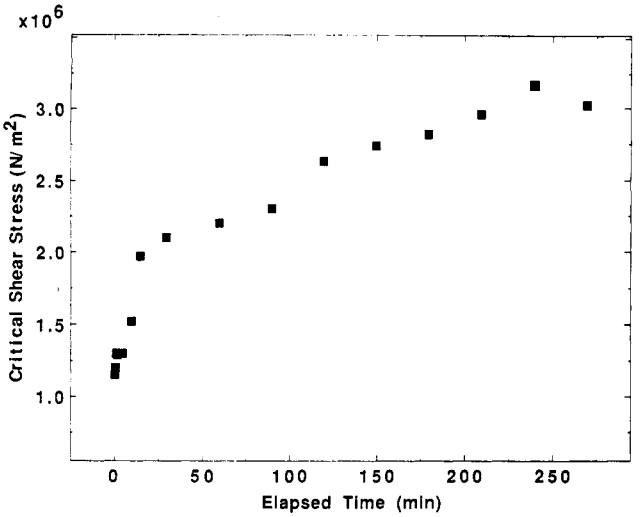

Figure 7. Critical shear stress plotted against elapsed time of the experiment for a PPMS sample (M_n = 2240) at film thickness 20 ± (1–2) Å and net normal pressure 0.8 MPa. Frequency of measurement was 1 Hz. Data taken from ref 12.

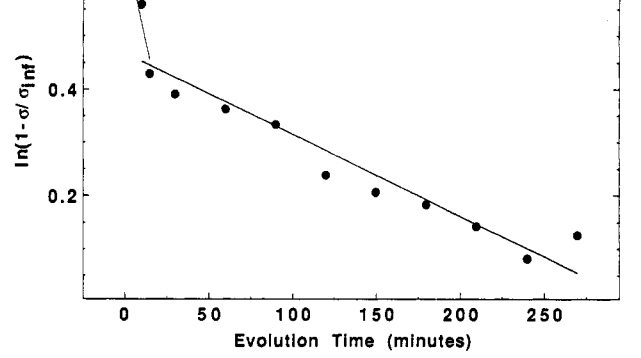

Figure 8. Same data as in Figure 7, replotted to show that the evolution of the critical shear stress may be described by two time constants. The quantity, $\sigma(t)$, is the critical shear stress. The quantity, σ_{inf}, is the plateau level of critical shear stress.

PDMS, to the point that PPMS does not crystallize in the bulk.[16] The glass transition temperature is −20 °C.[16] As we have discussed elsewhere,[12] the yield stress response was observed for this molecule also, showing that the capacity to crystallize in the bulk is not a precondition for a fluid to this response. Surface-induced crystallization would have been the likely origin of the yield stress response if PPMS had not displayed a yield stress, but experiment showed the contrary.

Figure 7 shows, for completeness, data taken from ref 12, which illustrates the time evolution of the critical shear stress. The film thickness of the sample was 20 Å; the net external normal pressure was 0.8 MPa. The time to reach a plateau in the critical shear stress was significantly longer than that for PDMS of similar chain length, with $\Gamma_{crit} \approx$ 660 min for M_n = 2240. This is consistent with the picture that the solidification behavior is associated with molecular reorganization, the PDMS chains of higher symmetry organizing more readily than the PPMS chains of lower symmetry.

Figure 8 shows a semilogarithmic plot of the same data plotted in Figure 7. The fractional deviation of the actual critical shear stress, $\sigma(t)$, from its plateau value at long times, σ_{inf}, is plotted logarithmically against linear time. It is evident that, just as shown in Figure 6 for PDMS, two time constants describe this data empirically also. The first time constant is 70 min; the second is 650 min. We speculate that the first apparent time constant may reflect rearrangements of chain conformation in response to the sudden change in film thickness. The longer time constant may reflect a glassy-like response tentatively alluded to earlier, an increasing difficulty of molecules to slip past one another. We emphasize that this interpretation is still highly speculative; experiments are currently underway to explore these matters further, in particular the dependence of the two time constants on the molecular weight.

Comparisons with Computational Results. Computer simulation is another strategy to explore these same questions of the dynamic behavior of polymer chains in confined geometries. It is true that the existing simulations of confined polymer chains,[3,4] discussed in the Introduction, are not strictly comparable to the present experiments. The simulations have probed equilibrium structures and diffusion rates, whereas the present experiments have explored the rates at which the confined liquid can reconstruct in response to applied mechanical stress. Nonetheless, it is interesting to compare the phenomena that emerge from these two such different approaches. Two points stand out.

The first point is that the experimental shear measurements of the viscous response illustrate that an enhanced pattern of energy dissipation can be relatively long-ranged, extending to a thickness of more than 70 Å and exhibiting an apparent divergence. This appears to contrast with the simulation findings that the changes in diffusion rates are relatively minor, at equilibrium at constant pressure. There are several possible origins of this apparent discrepancy. Our experimental procedure might play a role, the shear experiment itself *modifying* the structure of the film by inducing an orientation, as noted above. More generally, these results raise the possibility that the effective *dynamic* thickness of these layers may be significantly larger than the *equilibrium* thickness probed in the simulations. Further work will be necessary to decide these questions.

The second point, which stands out in comparison to the simulation findings, is that the available simulations show no evidence of the remarkable transition we observed from liquidlike to yield stress rheological response. (As we have noted, the solidlike response may reflect a liquid with relaxations slower than the experimental time scale.) This transition was found to occur at a film thickness significantly larger (by a factor of approximately 4–6) than the thickness of the chain segments. By contrast, the simulations show only relatively small perturbations in diffusion rates, and these occur at distances closer to the solid walls.

We note parenthetically that the thickness at the transition, which does not vary with the molecular weight of the chains, therefore does not appear to be related to the radius of gyration (the latter has been calculated for these chains by using rotational isomeric state approaches[24]).

These differences between experiments and simulations may in part reflect differences in the time scales probed in experiments and in simulations. A chain tightly adsorbed to the surface (i.e., one with an aggregate segmental adsorption energy $\gg kT$) would seem to have center-of-mass diffusivity governed by the rate at which the chain executes a random walk along the surface. At the film thicknesses of the present experiments, a significant fraction of the average chain can be shown to be bound to the surface, so one may expect these chains to display

dynamic responses governed by the rates at which the surface layer can reconstruct in response to the applied stress. The measured evolution in the critical shear stress suggests relaxations that occur over the time scale of hours. It would be difficult to extend simulations (currently performed over times not longer than nanoseconds) to these experimental time scales.

It is also possible that these different results may in part reflect some significant difference between the simulation models and the experimental systems. A particularly important difference appears to be that the simulations have been carried out at constant *volume*. Such simulations might therefore not detect a transition that, we have suggested above, may involve small changes in the volume in the system. In addition, atomic *structure of the confining walls* might play a role. Indeed, this was the conclusion in recent Monte Carlo simulations of atomic fluids confined between structured walls with the same periodicity as that of the fluid.[22,23] Both of these questions remain open at present and need to be addressed in future work in order to reconcile these two apparently disparate pictures.

Conclusions and Future Prospects

The principal observation we report here is that of two qualitatively different responses to shear of ultrathin polysiloxane films. In the liquidlike response, no critical shear stress was required to activate sliding motion. In the solidlike response, sliding motion did not occur unless a critical shear strength was exceeded. These observations are in qualitative agreement with our previous experiments[11,12] involving (nonpolar) liquids of hexadecane and of smaller molecules. The present observations, however, occurred at significantly larger film thickness. The observation of a fluid to solidlike transition therefore appears, at this stage, to be a general one.

The film thickness at the transition was found to depend on the history of the experiment but not on the molecular weight of the PDMS fractions. To observe that the thickness did not vary with molecular weight suggests that the eventual explanation of the structure which underlies the solidlike response will involve considerations of the local packing of segments. In this respect, it is possible to reconcile our observations with those of the recent computer simulations, which did not observe this transition,[3,4] by noting that the simulations were performed at constant volume and the experiments at constant pressure.

The times to accomplish the transition were on the order of seconds to minutes. The ensuing yield stress of the solidlike films were observed to increase over even longer times. These reorganization times are larger, by many orders of magnitude, than those of the isotropic liquids, which behave as Newtonian liquids at these temperatures and pressures.[16]

To observe such long times suggests that relaxation in these systems may be comparable to or longer than the experimental time scale. The shear rheology of these thin polysiloxane films is therefore exceedingly rich, complex, and dependent in its quantitative aspects on the history of the experiment.

It is clear that these experiments raise more questions than they answer. This problem has turned out to be more complex than might have been anticipated. This paper summarizes our initial observations and tentative explanations. Much more study, both experimental and theoretical, will be needed to understand the nature of the trapped structures which give rise to the yield stress phenomenon, the nature of the defects in these structures which accommodate the ultimate sliding motion, and the structure of these liquid films during the times that they do accommodate sliding. The present study summarizes the basic questions we have identified to date.

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