Nanorheology of Confined Polymer Melts. 2. Nonlinear Shear Response at Strongly Adsorbing Surfaces

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Received December 13, 1993. In Final Form: July 27, 1994.

The large-amplitude nonlinear shear rheology of polymer melts confined between strongly adsorbing surfaces (parallel plates of mica) was studied as a function of strain, frequency, and thickness of the polymer films. The shear strains varied from less than 0.1 (linear response) to over 30 (at which the film structure was strongly modified by the imposed shear). The measurements employed a surface forces apparatus modified for dynamic mechanical shear. The polymers were atactic poly(phenylmethylsiloxane) (PPMS), with chain lengths from 31 to 153 skeletal bonds. The nonlinear shear forces, decomposed into a Fourier series of harmonic frequencies, were always odd in the excitation frequency, as required by symmetry considerations. The in-phase and out-of-phase oscillatory shear responses at the same frequency as the excitation (the nonlinear storage and loss moduli \(G'_1\) and \(G'_2\), respectively) were analyzed. Four principal conclusions emerged. First, from the frequency dependence of \(G'_1\) and \(G'_2\) at constant strain, we conclude that relaxations were accelerated by large strain. Second, a marked decrease of both \(G'_1\) and \(G'_2\) was observed with increasing strain at constant frequency, except at the smallest film thickness, \(\approx 40\, \text{Å}\), where \(G'_2\) passed through a maximum with increasing strain but \(G'_1\) continued to display shear-thinning. Third, the critical strain for onset of nonlinear response increased with the excitation frequency. Fourth, at sufficiently large strains (larger than 10), the shear moduli were independent of polymer molecular weight (comparisons made at fixed film thickness) and appeared to reach limiting strain-independent levels at sufficiently large strains. This final observation contrasts sharply with the linear response and is consistent with shear-induced loss of interdigitation between opposed adsorbed polymer layers, consistent with the tendency toward slipage of adsorbed polymer layers over one another.

Introduction

In applications such as extrusion in polymer processing, lubrication in magnetic storage media, and polymer matrices filled with solid particles, confined polymers experience a large strain amplitude. It is therefore of practical significance to understand rheology of ultrathin films under these extreme conditions. For simple molecules this nonlinear rheology is relatively simple and can be interpreted as a shear thinning of the viscosity, even in confined geometries. In this paper we describe a more complicated response for long-chain molecules.

The accompanying paper considered the linear shear response of confined polymer melts—the condition under which the effects of sequential changes in shear amplitude were additive. Here, in response to excitation at some frequency, the response contained only the input frequency. But as strains increase, the dynamics of a material's response become nonlinear and higher odd-order harmonics are generated. The even-order harmonics are zero because the stress is an odd function of strain.

And the moduli can be represented as

\[
G'_n(\omega,\gamma_0^2) = \sum_{m=n}^{\infty} \gamma_0^m G'_m(\omega) G'_n(\omega,\gamma_0^2) = \sum_{m=n}^{\infty} \gamma_0^m G'_m(\omega)
\]

\[
G''_n(\omega,\gamma_0^2) = \sum_{m=n}^{\infty} \gamma_0^m G''_m(\omega) G''_n(\omega,\gamma_0^2) = \sum_{m=n}^{\infty} \gamma_0^m G''_m(\omega)
\]

for as many harmonics as can be identified in the response. Thus, one expects that nonlinear behavior with increasing strain during a cycle of oscillation should manifest itself in the appearance of odd-order harmonics in dynamic shear experiments.

Experimental Section

The experimental setup employed a surface forces apparatus modified for sinusoidal shear excitation, as described in the preceding paper. Narrow distribution fractions of atactic poly(phenylmethylsiloxane) (PPMS) of number-average molecular weights 2240 g mol\(^{-1}\) (polymer A), 4550 g mol\(^{-1}\) (polymer B), and 10 560 g mol\(^{-1}\) (polymer C) were studied. Detailed characteristics of these polymer samples were described in Table 1 of the preceding paper.

It may be natural to question whether shear motion of large amplitude maintains a strictly uniform separation. While normal forces should in principle increase the separation by some amount, such changes were less than the experimental thickness resolution of 1–2 Å. In addition, a simple calculation based on the arc-angle subtended during a cycle of oscillation shows that the amplitudes of oscillation resulted in negligible liftoff during each swing. It was negligible because the deflection of the cantilever spring, which imposed normal forces, vastly exceeded the vertical motion of the piezoelectric bimorphs during oscillations.

The rheological model of the glue layer, described in ref 5, was shown to remain valid at these large shear amplitudes. This was shown since calibrations of the glue layer did not depend on the shear amplitudes. Furthermore, inspection of the assumptions of the rheological model shows that the model remains valid for analyzing nonlinear behavior.
functions has been discussed by Matauda and co-workers.\textsuperscript{6} This difference waveform was composed of higher odd-order harmonics, mostly third harmonics.

The difference waveform—The actual waveform with subtraction of the fundamental frequency, 0.052 Hz. The difference waveform was composed of higher odd-order harmonics, mostly third harmonics.

Figure 1. Example of raw data. (Top panel) Shear response waveform of polymer A, film thickness 27 Å, plotted versus time. The drive oscillation frequency is 0.052 Hz with amplitude 200 Å. (Bottom panel) Waveform shown in top panel after subtraction of the fundamental frequency, 0.052 Hz. The difference waveform was composed of higher odd-order harmonics, mostly third harmonics.

The polymers were confined between freshly cleaved mica surfaces. The polymers wet these surfaces with a contact angle of zero. We estimate the adsorption strength to mica as 3–5kT per repeat unit, as described elsewhere.\textsuperscript{7} As described in the accompanying paper, this is a conservative estimate of the actual adsorption strength.\textsuperscript{8}

Results

Figure 1 (top) displays, for polymer A, a voltage waveform of the raw output data. The driving oscillation was \( \omega_1 = 0.052 \) Hz with strain amplitude of 200 Å. The output waveform was not, however, only at frequency \( \omega_1 \). The difference waveform—the actual waveform with frequency \( \omega_1 \) subtracted—is shown in Figure 1 (bottom). This difference waveform was composed of higher odd-order harmonics, mostly third harmonics of frequency \( \omega_3 = 0.156 \) Hz. The Fourier components are presented in Figure 2. Odd-order harmonics up to fifth order could be resolved, while the even-order harmonics were vanishingly small due to symmetry considerations.\textsuperscript{1,6}

The physical meaning of these nonlinear viscoelastic functions has been discussed by Matauda and co-workers.\textsuperscript{5}

\begin{align}
\text{Figure 2. Fourier components of the waveform shown in Figure 1. Odd-order harmonics up to fifth order can be resolved.}
\end{align}

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The work done on the system from time 0 to \( t \) is

\begin{align}
W &= \int_0^t \sigma \gamma \, dt
\end{align}

The moduli \( G_1'(\omega_1) \) and \( G_1''(\omega_1) \) are the analogues in nonlinear viscoelasticity of \( G(\omega) \) in linear viscoelasticity. They are effective measures of the ability of the materials to store and to dissipate energy.

Substituting eq 1 into eq 3 shows that the energy dissipated over one complete cycle of oscillation is determined solely by \( G_1'' \). In contrast, the elastic energy stored and released in one cycle at frequency \( \omega_1 \) is influenced by higher-order harmonics. However, response at the fundamental frequency (denoted \( G_1' \)) dominated in the experiments described below, because of the large voltage amplitude of the first harmonic relative to those of the higher-order odd harmonics shown in Figure 2. To a first approximation, then, \( G_1' \) can be regarded as the elastic response of the material to shear. The uncertainty introduced by this approximation is at most 14% in the experiments described in this paper.

It must be emphasized that, for a complete description of the stress, higher-order harmonics are required. Unfortunately, the phase shifts of these harmonics were not resolved in this study due to the frequency-dependent phase shifts introduced by filters in the preamplifier electronics.

Strain Dependence. Figure 3 shows the strain dependence of the storage modulus, \( G' \), for a film of polymer A of thickness 27 Å, measured at 0.26 and 130 Hz. Linear behavior held up to higher strains, the higher the frequency. Presumably this reflected the increased difficulty, at the higher frequencies, of achieving a distorted structure over the experimental time scale.

The corresponding voltage amplitudes of the third-harmonic response, normalized by the voltage amplitude of the fundamental response at these two frequencies, are shown in Figure 4. For the lower frequency, this normalized amplitude of the third harmonic became finite at a strain of \( \approx 0.8 \) and passed through a maximum at a strain of \( \approx 4 \). Similarly, for the higher frequency, the rise of the third harmonic began at a strain of \( \approx 3 \); and no decrease in amplitude was evident over the strain range which was studied. The rich strain-dependence of this harmonic response is worthy of further study.

Conceptually, if one examines the dynamics at various nonlinear strain amplitudes on a fixed time scale, the

\begin{align}
\text{Figure 3. Strain dependence of the storage modulus, for polymer A at film thickness 27 Å. Measurements (0.26 Hz, circles; and 130 Hz, squares) are plotted versus strain amplitude on log-log scales. The storage modulus is denoted } G_1' \text{ because, as discussed in the text, it was calculated from the fundamental component of response.}
\end{align}
thicknesses. Strain is defined as oscillation amplitude normalized by film thickness. The loss modulus response reflects the dynamical structure and relaxation processes perturbed by strains on that time scale. "The onset frequency for the shear thinning of the storage modulus in the frequency spectrum increased with strain amplitude. We interpret this to indicate that, at higher frequencies, the correlations between the confined molecules did not have time to relax. However, at lower frequencies the molecules were less correlated on these long time scales; shear thinning started at lower strain amplitudes. A higher strain amplitude was needed to disengage the strongly correlated molecules, the higher the frequency of measurement."

**Effects of Confinement.** We now fix the strain amplitude at 200 Å and the frequency at 1.3 Hz. Figure 7 compares the resulting nonlinear viscoelastic moduli, G′ and G′′, with their linear counterparts as the film thickness was varied. G′ was less than G′′ in every case, except for the very thinnest films where G′ ≈ G′′. Otherwise stated, the ability of the confined polymer melt to store elastic energy was drastically hampered at high strain amplitude except when the molecules were strongly correlated in the thinnest films.

The loss modulus, G′′, was small compared to G′ at large separations. However, there was a crossover film thickness, beyond which G′′ > G′. In the thinnest films both G′ and G′′ decreased with decreasing film thickness. One observes that the shear thinning of the storage modulus, and the crossover from shear thinning to shear thickening of the loss modulus, depended upon both frequency and strain amplitude.

**Frequency Dependence of Nonlinear Moduli.** First we fix the strain amplitude at 200 Å and compare at strains of 1–5 and decreased slowly when the strain was raised still more. The shear-thinning or shear-thickening responses are considered further below, in the discussion of Figures 9 and 12. The associated strain dependence of the storage modulus, G′, is plotted in Figure 5 (bottom). In contrast to G′′, this measure of the energy stored and recovered at frequency ω decreased monotonically with increasing strain, regardless of the film thickness. For the thinnest films, the dynamics became quite complex due to strong correlations between the molecules and the surfaces. It is of interest to investigate the dynamics in detail by varying both strain and frequency. Figure 6 presents the storage modulus, plotted versus frequency on log-log scales, of polymer A confined to the small film thickness of 27 Å. The storage modulus remained in the linear viscoelastic regime up to a shear amplitude of 12 Å (strain ≈ 0.5). The onset frequency for the shear thinning of the storage modulus in the frequency spectrum increased with strain amplitude.

We interpret this to indicate that, at higher frequencies, the correlations between the confined molecules did not have time to relax. However, at lower frequencies the molecules were less correlated on these long time scales; shear thinning started at lower strain amplitudes. A higher strain amplitude was needed to disengage the strongly correlated molecules, the higher the frequency of measurement.
Figure 7. Dependence on film thickness of the nonlinear (filled symbols) and linear (hollow symbols) shear moduli of polymer B measured at 1.3 Hz. Data are plotted on logarithmic scales versus linear film thickness. The nonlinear moduli were measured at oscillation amplitude 200 Å, and the linear moduli at oscillation amplitude 2 Å. Squares: $G''$ and $G'''$. Circles: $G'$ and $G'_1$.

Figure 8. Frequency dependence of the nonlinear (filled symbols) and linear (hollow symbols) shear moduli of polymer B at film thickness 90 Å. Measurements are plotted on log-log scales versus excitation frequency. Nonlinear moduli were measured at 200 Å amplitude, and linear moduli at 2 Å amplitude. Squares: $G''$ and $G'''$. Circles: $G'$ and $G'_1$.

Figure 9. Frequency dependence of the nonlinear (filled symbols) and linear (hollow symbols) shear moduli of polymer B at film thickness 62 Å. Measurements are plotted on log-log scales versus excitation frequency. Nonlinear moduli were measured at 200 Å amplitude, and linear moduli at 2 Å amplitude. Squares: $G''$ and $G'''$. Circles: $G'$ and $G'_1$.

Figure 10. Frequency dependence of the nonlinear (filled symbols) and linear (hollow symbols) shear moduli of polymer B at film thickness 42 Å. Measurements are plotted on log-log scales versus excitation frequency. Nonlinear moduli were measured at 200 Å amplitude, and linear moduli at 2 Å amplitude. Squares: $G''$ and $G'''$. Circles: $G'$ and $G'_1$.

The frequency spectrum of the linear and nonlinear moduli at various extents of confinement. Figure 8 shows this comparison for polymer B at 90 Å thickness. One observes that $G_{1''}$ was an order of magnitude less than $G''$, but that the slope on the frequency scale was approximately unity, indicating terminal zone behavior. We interpret this to indicate that the high strain amplitudes somehow weakened the polymer; the material was less viscous than at small strain amplitudes. This probably reflects orientation of the structure, in analogy to shear thinning in steady flow.

Figure 9 exhibits the nonlinear viscoelastic moduli of polymer B at film thickness 62 Å, plotted against angular frequency. Here the nonlinear $G''$ was severely shear-thinned relative to $G'$ at low frequencies (<1 rad s⁻¹) but gradually approached $G'$ at higher frequencies. The nonlinear $G_{1''}$ crossed $G''$ at angular frequency 100 rad s⁻¹. The slope of the $G_{1''}$ curves on the log-log plot was roughly 0.5, which is obviously a far weaker dependence than the characteristic slope of unity for the terminal zone of linear viscoelasticity, but a much stronger dependence than for the $G'$ curves over this same range of frequency. This suggests that, at this film thickness, the measurement frequencies always exceeded the longest inverse relaxation time of the confined system.

Figure 10 shows the nonlinear viscoelastic moduli of polymer B at the still-smaller film thickness of 42 Å. As at 62 Å, $G_{1''}$ was thinner than $G'$ at low frequencies but overlapped with $G'$ at angular frequencies greater than 20 rad s⁻¹. The crossover from shear thinning to shear thickening of $G_{1''}$ shifted to a lower angular frequency than at the larger film thickness of 62 Å, only 1 rad s⁻¹. The strain softening in the liquidlike regime may be interpreted as accelerated relaxation at high strain or high stress. It is interesting to notice that the nonlinear
Namrheology into play. The measurements are plotted versus strain on log–log scales. Strain is defined as oscillation amplitude normalized by film thickness. Squares: polymer A. Circles: polymer B. Diamonds: polymer C. Storage moduli are shown in the top panel, and loss moduli are shown in the bottom panel.

\(G''_1\) was shear-thinned at low frequencies (<1 rad s\(^{-1}\)) and shear-thickened at higher frequencies. The concept of strain-accelerated relaxation then no longer applied cleanly; another relaxation mechanism evidently came into play.

From a molecular point of view, strain softening can arise from enhanced disengagement between correlated molecules with the applied strain.\(^8\) From this point of view, the overlapping frequency responses of the nonlinear \(G'_1\) and \(G''\) in these plots may indicate a time scale over which such disengagement could not be accomplished; appreciable reduction of the storage modulus occurred only at longer time scales.

At short time scales, chain dynamics were dominated by short-range local relaxations; while at long time scales, they were influenced by long-range global relaxations. These slower global relaxations were the first to be accelerated by the strain, presumably by breaking of some kind of correlations between the molecules. In contrast, appreciable strain softening at high frequency occurred within the experimental frequency range only for the thinnest films.

Figures 7 and 8 show that the onset of the overlap frequency of the storage modulus, and the crossover frequency from thinning to thickening of the loss modulus, both shifted to lower frequencies with decreasing film thickness. Thus as the structure and correlation became stronger, it required a longer time to disengage the molecules even at high strains.

**Effects of Molecular Weight.** Figure 11 shows the storage and loss moduli of polymers A–C confined at the fixed film thickness of 60 ± 3 Å, plotted versus strain amplitude at 1.3 Hz: the higher the molecular weight, the higher the linear viscoelastic moduli. Startlingly, the nonlinear moduli converged at the highest strain amplitude of 50. To observe that dynamics are independent of molecular weight is remarkable. This also suggests some kind of loss of correlation between molecules.

The frequency dependences in Figure 12 support this idea. The nonlinear storage and loss moduli at thickness

60 ± 3 Å (measured at a constant strain amplitude of 200 Å) converged more or less for all of the frequencies studied, for all three samples.

This suggestion that relaxations at high strain were independent of molecular weight also held true of polymer A and polymer B confined to 50 Å, as shown in Figure 13. (However, polymer C had reached such a steep repulsion by this point that it could not be reduced to 50 Å thickness; cf. Figure 6 of the accompanying paper.\(^9\) Figure 13 shows the convergence of the storage and loss moduli (at strain amplitude 200 Å) over all of the frequencies studied.

This independence upon molecular weight also held for still thinner films. Figure 14 shows the strain dependence at 1.3 Hz of the storage and loss moduli of polymers A and

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responses, we begin with the linear response. The coelastic behavior; the linear response, one investigates the dynamics as the dynamics under various strain amplitudes outside in the discussion earlier in this paper from the frequency viscoelastic response require knowing the constitutive harmonics are small compared to the linear response.

Figure 14. Strain and molecular weight dependence of the nonlinear shear moduli at fixed film thickness, 44 ± 3 Å, and fixed excitation frequency of 1.3 Hz. The measurements are plotted against strain on log-log scales. Strain is defined as oscillation amplitude normalized by film thickness. Squares: polymer A. Circles: polymer B. Storage moduli are shown in the top panel, and loss moduli are shown in the bottom panel.

B confined to 44 Å film thickness. The curves for the two samples track one another. It is striking to notice that the nonlinear loss modulus GI" increased by a factor of approximately 10 as the strain was raised, passed through a broad peak at strains of 1–5, and decreased slowly toward the linear value at strains from 5 to 30.

Approximate Relaxation Modulus. When response is linear, as in the preceding paper, then the methods to convert from the frequency to the time domain are well established. Fundamental calculations of nonlinear viscoelastic response require knowing the constitutive equation, and this is not known in this case. But as a guide to intuition, it is appealing to estimate the nonlinear relaxation modulus by the known equations appropriate to linear viscoelasticity. Certainly, this approximation is very crude. It neglects all the nonlinear harmonics. However, it can reveal some features of the material behavior at large strains so long as the nonlinear harmonics are small compared to the linear response.

Figure 15 shows the calculated relaxation modulus of 31 bond PPMS confined to 27 Å, plotted versus time at various strains. The relaxation modulus is calculated from GI(1) (Figure 6) and GI(2) by applying Schwarzl’s formulas to the response at frequency ᵔ, and it thus must be regarded as an “effective” relaxation modulus. The marked shear thinning of the relaxation modulus, inferred in the discussion earlier in this paper from the frequency response, shows up blatantly in this representation and may be compared with the linear relaxation moduli in Figure 15 of the accompanying paper.

Discussion and Conclusions

High strain amplitudes decisively change the structure and dynamics of confined polymer melts. If one probes the dynamics under various strain amplitudes outside the linear response, one investigates the dynamics associated with the perturbed structure.

In seeking to interpret these prominent nonlinear responses, we begin with the linear response. The accompanying paper analyzed that response and presented the tentative physical picture of interdigitated opposing polymer layers, each adsorbed to a solid surface, resulting in a structure and correlation that were interpreted as enhanced entanglement. This situation was considered the simplest to analyze because the deformations were so small as not to deform the structure of the confined chains. Clearly, this broke down severely under the influence of strain. One is then interested to inquire into how the original undeformed structure was broken up and, conversely, into understanding what new shear-induced structures may have developed.

The measurements suggest that molecular relaxations were accelerated by large strains. Below strain amplitudes of ~0.1 (1.3 Hz), linear responses prevailed, but the molecular organization apparently became gradually less correlated at higher strain amplitudes. The critical strain amplitude for the onset of nonlinear response increased with increasing frequency. This is qualitatively consistent with the naive view that structural reorganizations at higher frequencies could not be accomplished over the experimental time scale. The observation may also indicate that not only absolute strain but also the peak strain rate encountered during the sinusoidal deformation and the peak stress sustained during a cycle of oscillation play a part in determining the onset of nonlinear response. If peak strain rate is the fundamental quantity, then one is led to interpret the nonlinear response to indicate that the rate of the experiment exceeded a characteristic inverse structural relaxation time. But if peak stress during a cycle of oscillation is the fundamental quantity, one is led to view nonlinear response as a rupture phenomenon. A rich area for study is offered by the possibility that, in future work, one might be able to decide between these two possibilities.

Major strain dependence is shown from the analysis of GI(1) and GI(2), which are proportional to the energy stored and lost during oscillation at the fundamental frequency, respectively. In every case the modulus GI(1) decreased with increasing strain, indicating loss of structure. Likewise, the modulus GI(2) decreased with increasing strain, so long as the films were not too thin (>60 Å thick). This contrasts with typical experience in colloidal suspensions, and we speculate that the phenomenon reflected lessened interpenetration of the opposing layers. In this

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view, interdigitation slackened with increasing strain.

It is provocative to notice, at the highest strains, the loss of molecular weight dependence of the nonlinear moduli at fixed thickness. This contrasts with the linear response and is consistent with the conclusion of shear-induced loss of interdigitation between opposing polymer layers. The viscoelastic response would then reflect the slippage of opposed layers past one another and should be independent of molecular weight.

We do not favor explanation in terms of detachment of polymer from the solid surface, since mica has a high-energy surface and certainly interacts strongly with the polymer chains. It is then plausible to expect that a weakest link elsewhere within the polymer film will break first. Accordingly, we tentatively attribute the phenomenon to the shear-induced loss of interdigitation between opposing polymer layers. At any rate, it is essential to note that the dissipative stress continued to climb with increasing peak velocity (peak velocity is the product of shear amplitude and shear frequency). This contrasts acutely with the distinct velocity independence which characterizes the slip of confined films of smaller molecules.

Another salient observation is the thixotropy of the thinnest films—the increase of $G''$ by approximately an order of magnitude. At the same time that $G''$ decreased with increasing strain, $G''$ increased and passed through a broad peak at strains of $1-5$ and decreased at still larger strains toward the original linear value. The nonlinear loss modulus eventually even crossed the nonlinear storage modulus. This appears to be typical of highly compressed systems—not intrinsically a polymer phenomenon. Thus, although one might speculate that the observation stems from the rupture of bridging of chains between the two solid surfaces, behavior of this sort is also typical when suspensions of colloidal spheres experience shear at high amplitude. In addition, this laboratory's other work in progress, similar in scope to that presented here for polymers, also reveals thixotropy of $G''$ for alkanes and other small-molecule liquids when they are confined to ultrathin films.

What might be the underlying structural changes? In the yield of bulk solids, an increase of volume appears to be the mechanism. Similarly, increases in film thickness (although less than the experimental resolution of $1-2$ Å) are reasonable to expect in the present systems and indeed are predicted in computer simulations of confined liquids. An interesting consequence is that this should be accompanied by forces which act in the direction normal to the sliding direction. In future work it would be interesting to explore these normal forces.

In summary, this paper and the accompanying one have compared the linear and nonlinear shear rheology of films of amorphous, flexible polymer chains, confined between adsorbing surfaces to thicknesses comparable to the unperturbed radii of gyration. The amplitudes of sinusoidal excitation were varied from a few angstroms (linear response) to up to 800 Å (strain larger than 30). It is clear that, because the films were so thin, enormous strains were produced by seemingly small deformation amplitudes. Thus, as noted in the Introduction, nonlinear responses must be very common in physical situations where polymer films are so thin. The general theme of the experimental findings is to suggest extensive shear-induced reorganization, with conspicuous rheological consequences.

Acknowledgment. We are indebted to J. F. Douglas, J. D. Ferry, G. Reiter, and K. Schweizer for comments and discussions and to S. J. Clarson for donating the PPMS samples used in this study. We thank the Exxon Corp. for generous assistance. G.A.C. acknowledges support from Grant NSF-MSS-92-02143. We acknowledge support of the National Science Foundation through the Materials Research Laboratory at the University of Illinois, Grant NSF-DMR-89-20538.