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Viscosity of entangled polystyrene thin film melts: Film thickness dependence

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We determined the low-shear effective viscosity of *entangled* polystyrene thin film melts, in the thickness range of $27<h<100$ nm, on SiO_x/Si substrates. This was accomplished using a method based on the notion that thin liquid films can become unstable and rupture due to defects or to destabilizing, long-range van der Waals interactions (dewetting). The holes that are created in the film subsequently grow at a rate determined by a balance between the capillary driving forces and the viscous resistive forces. Based on the velocity of growth of holes on the substrate, we show that the viscosity decreases appreciably with decreasing thickness for $25<h<50$ nm. These results are consistent with studies which suggest that the glass transition of *entangled* polystyrene thin film melts on SiO_x/Si substrates exhibit an apparent decrease with decreasing film thickness over the same range of h.

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INTRODUCTION

Structure and dynamics at polymer surfaces and in thin polymer films can differ substantially from the bulk [1–25]. It is well understood that chain segments in the vicinity of the free surface are more mobile than those in underlying layers [2,7,8]. On the other hand, chain segments at the polymer/substrate interface are less mobile than chains in upper layers, particularly in the presence of a strongly interacting substrate [15–17]. In fact, highly confined chains exhibit anisotropic segmental mobility in thin films. For example, experiments reveal that the segmental mobility normal to the surface decreases while the mobility parallel to the surface increases [12,15,16,24]. In thin films, changes in properties such as the glass transition, chain diffusion, and the viscosity can be manifestations of the polymer-substrate, polymer-surface interactions, and confinement effects. These issues are far from understood and they present new challenges for which new rules must be developed.

In this paper we are primarily concerned with the manner in which the viscosity η of thin films varies with film thickness h. Few measurements of the film thickness dependence of η exist. Surface force measurements of the viscosity of polystyrene films, for example, indicate that η increases with decreasing film thickness when the distances of separation are of the order of nanometers to a few tens of nanometers apart [25]. The increase of the viscosity with decreasing film thickness would appear to be at odds with the decrease in T_g reported by a large body of researchers [4,17–23]. However, in the surface force experiments, both interfaces of the film are constrained by hard substrates. As a result, these measurements do not provide meaningful information about the more common, asymmetric situation where one of the interfaces is a free surface. Clearly, the nature of the interactions of the polymer chains at the interfaces in these tribological measurements would be important, particularly when the distance of separation was of the order of nanometers or tens of nanometers. In light of the influence of interfacial interactions on the mobility of chains near constrained interfaces vs unconstrained interfaces (free surfaces), the behavior of the symmetric and asymmetric cases should be different.

We determined, indirectly, a film thickness dependence of the low-shear *effective* viscosity of thin polystyrene films in the thickness range $25<h<75$ nm. We used a method based on the premise that thin polymer films on surfaces can become unstable and rupture, thereby creating holes [26–47]. The growth rate of the holes, within the experimental regime of interest to us in this paper, is determined by a balance between the capillary driving forces and viscous resistive forces. The viscosities determined from these measurements are influenced largely by the lateral translational dynamics of the chains on the substrate.

EXPERIMENTAL SECTION

The samples were prepared by spin coating solutions of toluene and polystyrene of molecular weight $M_w=130$ kg/mol ($M_w/M_n\leqslant 1.06$) onto silicon substrates. The glass transition temperature of high molecular weight polystyrene (PS) is 100 °C. The substrates had native SiO_x layers of 2 nm, as measured by spectroscopic ellipsometry. Hereafter we identify this as the $PS/SiO_x/Si$ system. The thickness of the polystyrene films, ranging from 25 to 102 nm, was measured by spectroscopic ellipsometry as well as by atomic force microscopy (AFM). AFM was also used to ensure that the surfaces of the films were smooth after preparation and that rupturing occurred during annealing. The system was subsequently annealed for various times at 170 °C in a vacuum oven. Successive images of the same regions of the samples, quenched to room temperature, were taken at periodic intervals using AFM.

RESULTS AND DISCUSSION

For films thicker than 74 nm local depressions, or dimples, developed at locations throughout the film. These depressions increased in depth but did not impinge on the surface even after days of annealing. When the films were in the thickness range $27<h<74$ nm, cylindrical holes (exposed substrate) appeared throughout the film, Fig. 1, after a few minutes of annealing. An AFM line scan of a typical hole is shown in Fig. 2. We note that while the hole radius

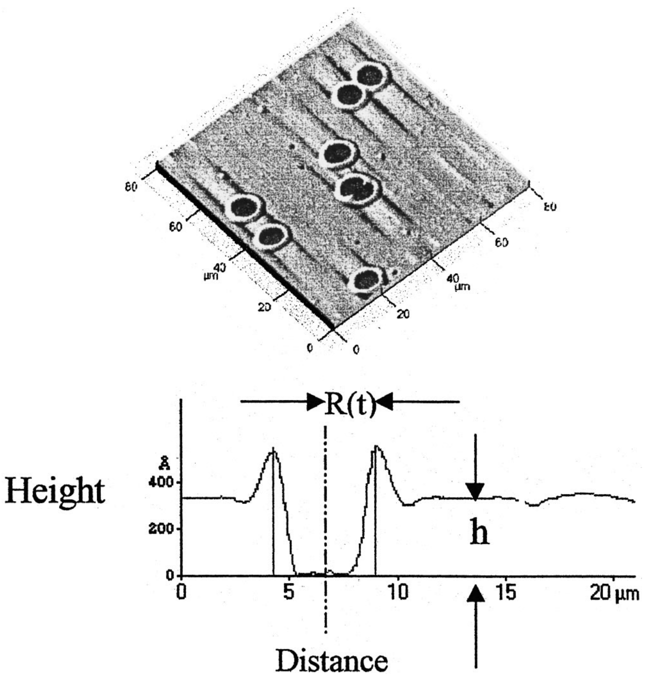

FIG. 1. A typical AFM image of a sample, accompanied by line scans. The radius of the hole is identified.

$R(t)$ increased with time in each sample, the dynamic angle of contact θ_d remained relatively constant during this stage and was smaller than the equilibrium contact angle, as expected.

Generally, the rupture of thin films can be understood based on the following. For sufficiently thin films, the excess free energy of interaction can be expressed as combination of long- and short-range interactions, $\Delta G = -A/(12\pi h^2) + \phi(h)$ [34,41,46]. The first term represents the van der Waals interaction between the liquid/vapor and liquid/substrate interface and $\phi(h)$ represents the potential associated to the short-range interactions. A is the Hamaker constant of the substrate/polymer/vacuum system. Thermal fluctuations at the polymer/vacuum interface can spontaneously become amplified when the disjoining pressure $\Gamma = -\partial\Delta G/\partial h > 0$. While the driving force for this process is the disjoining pressure, a Laplace pressure, associated with the surface tension γ and the local radius of curvature, attempts to dampen the fluctuations. If the disjoining pressure is more dominant than the Laplace pressure, then fluctuations can subsequently grow and impinge on the substrate, creating different patterns, reflecting fluctuations in the local film thickness. Depending on the curvature of the free energy with film thickness, spinodal patterns [33,38,40] or holes [29,30,38] have been observed.

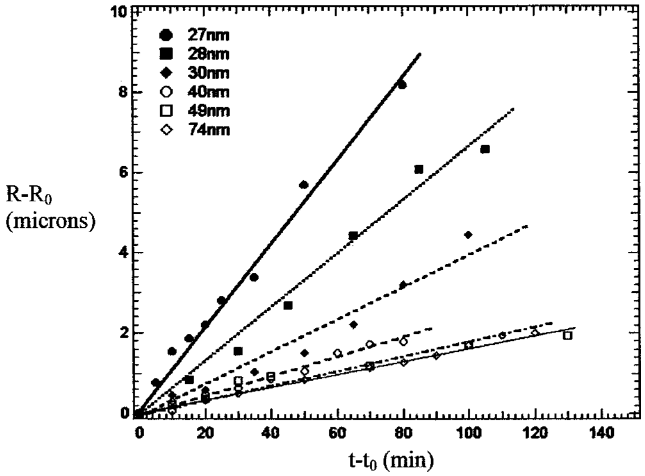

FIG. 2. The radii of the holes in each film were observed to increase linearly with time for each film thickness.

Rupturing of thin films may also occur due to the presence of defects. Here local gradients in interfacial tension occur in the presence of impurities close to the surface of the film. These gradients in interfacial tension generate a local flow that leads to the formation of local depressions (dimples) in the film. If the local thickness of the film decreases below a certain value, the energy barrier for the formation of a hole is overcome, resulting in this heterogeneous nucleation process. This happens when $\gamma_{\rm pv} d^2$ (d is the depth of the local depression) is comparable to $k_B T$, k_B is the Boltzmann constant and T the temperature [26,47]. This nucleation event (formation of dimples) is not dependent on the original film thickness. Local depressions nucleate randomly throughout the substrate and if the film is sufficiently thin, then rupturing (hole formation) occurs.

When the depression impinges the substrate, creating a hole, the driving force for hole growth is the spreading coefficient S [32], where coefficient $S = \gamma_{\rm sv} - (\gamma_{\rm sp} + \gamma_{\rm pv})$, where $\gamma_{\rm sv}$, $\gamma_{\rm sp}$, and $\gamma_{\rm pv}$ are the substrate/vacuum, substrate/polymer, and polymer/vacuum interfacial tensions, respectively. An unstable film will eventually form droplets on a substrate provided that $S < 0$. The hole growth rate dR/dt is constant when the capillary driving forces are balanced by the frictional (viscous) forces. During this stage, the dissipation of energy occurs primarily at the substrate/polymer interface and a rim develops at the periphery of the hole, as chains accumulate there and the radius increases as [32]

$$R(t) - R_0 \approx \frac{|S|}{\eta}\left(\frac{b}{h}\right)^{1/2}(t - t_0). \qquad (1)$$

In this equation, the time t_0 is the time that the hole impinges on the substrate and R_0 is the hole radius at time t_0. The value of η in this equation corresponds to an average viscosity of the film in the vicinity of the edge of the hole. The slippage length is $b = aN^3/N_e{}^2$, where a is the monomer length [48,49] and N_e is the number of monomers between entanglements. Polystyrene of molecular weight 130 kg/mole has a slippage length $b = 17.5\ \mu$m with $a = 3.10^{-4}\ \mu$m, $N = 1250$, and $N_e = 183$ ($M_e = 19$ kg/mol for PS). Equation (1) is valid for $(bh)^{1/2} < R < R_c = b = 17.5\ \mu$m, and for $R \gg L$, where L is the rim width, which are always the case for the conditions in our study. During the later stage where $R > b$, $R \propto t^{2/3}$, because the size of the rim L increases ($L \propto t^{1/2}$), thereby increasing the frictional resistance to growth, while the driving force remains constant.

This paper is exclusively concerned with the time dependence of $R(t)$ in linear growth regime of cylindrical holes

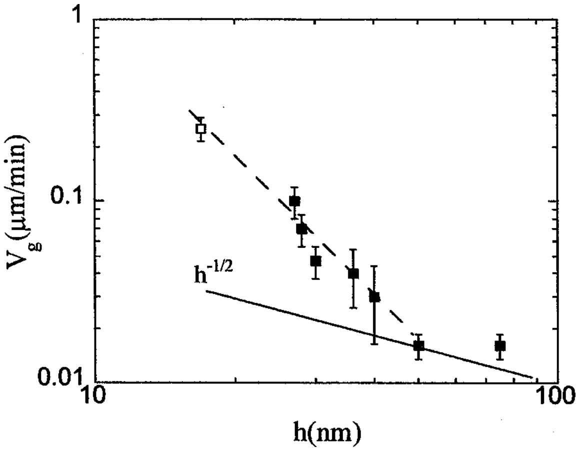

FIG. 3. The velocity of growth is shown to increase much more rapidly with film thickness than the $h^{-1/2}$ for $h<50$ nm. The solid line has a slope on $-\frac{1}{2}$ on this graph.

($27<h<74$ nm) on the SiO_x/Si substrates. Based on the data in Fig. 2, $R(t)$ increases linearly with time. Second, the growth rate $V_g = dR/dt$ decreases with increasing film thickness, as shown in Fig. 3. In fact, $V_g \propto h^{-k}$, where $k>1/2$ for the range of thickness $h<50$ nm. For $h<50$ nm, V_g increases at a considerably faster rate than that predicted by Eq. (1). Since the driving force for hole growth S is a constant and b is constant, the discrepancy between the theoretical prediction and our experimental result is reconciled by the fact that η decreases with decreasing thickness for $h<50$ nm, as discussed in detail below.

The viscosity in these thin films can be estimated from our data using Eq. (1), $\eta = \{(|S|b^{1/2})/[V_g(h)h^{1/2}]\}$, where $b = 17.5$ μm and $|S| = |\gamma_{lv}[\cos(\theta_e)-1]| = 5.75$ mJ/m^2 ($\gamma_{lv} = 31.8$ mJ/m^2 and $\theta_e = 35°$ and $\theta_d = 5.5°$ for this substrate). The effective viscosities determined from our data are plotted as a function of film thickness in Fig. 4, where they are shown to decrease monotonically with decreasing thickness for $27<h<50$ nm.

The trends in these data are consistent with observations that T_g of polystyrene films, in the same range of thickness, on SiO_x exhibits an apparent decrease with decreasing film thickness [4]. Keddie, Jones, and Cory [4] proposed an empirical equation to fit the decrease in T_g with decreasing thickness.

$$\frac{T_g(h)-T_g(\infty)}{T_g(\infty)} = -\left(\frac{\alpha}{h}\right)^{\delta}. \tag{2}$$

In sufficiently thick polystyrene films, $T_g(\infty) = 373.8$ K [4,50] and the constants α and δ are, respectively, $\alpha = 3.2$ nm and $\delta = 1.8$. Therefore, the effective temperature above the glass transition changes from $T - T_g$ to $T' - T_g$, where $T' = T + T_g(\infty)(\alpha/h)^{\delta}$. Thus, each successively thinner film in the regime $25<h<50$ nm is at a higher effective temperature $T'(h)$ above the glass transition. Larger effective mobilities are consistent with conditions of higher effective temperatures above the glass transition.

In order to be consistent with Eq. (2), we performed a similar analysis for the thickness dependence of the viscosity

$$\frac{\eta(h)-\eta(\infty)}{\eta(\infty)} = -K\left(\frac{\alpha}{h}\right)^{\delta}, \tag{3}$$

where α and δ are the same as those used to fit the T_g data. In this equation, $K = 35$ accounts for the fact that the decrease in the viscosity with film thickness is considerably larger than that of the glass transition temperature. In view of the above considerations, the viscosity measured for thin films in this paper is, therefore, an average viscosity and the fact that it decreases with decreasing film thickness reflects the dominant influence of the lower free surface viscosity. Neutron scattering measurements of thin polymer films show evidence of a decrease in the entanglement density with decreasing film thickness, which would be consistent with an enhanced mobility with decreasing film thickness [6].

These data further indicate that $\eta(\infty) \sim 2.5\times10^8$ P, which is considerably larger than the bulk viscosity at this temperature for this molecular weight $\eta = 2.5\times10^5$ P [50]. Some time ago, the following equation was proposed by Redon *et al.* to describe the velocity of a liquid dewetting a substrate assuming nonslip conditions, where the contact angle is small [52]:

$$V_g^{\text{nonslip}} = k(\gamma/\eta)\theta_e^3.$$

Shull and Karis later showed that the equation was generally applicable for larger contact angles and the angle of contact is expressed in degrees, then $k = 3.2\times10^{-8}$ (deg)$^{-3}$ [53]. While this equation is generally not believed to be applicable to entangled long-chain polymers, that may undergo slip, it predicts a more reasonable value for $\eta(\infty) \approx 9\times10^4$ P. This value is smaller than the bulk value yet within a factor of 3 of it. The large discrepancy between the two values of $\eta(\infty)$ extracted using Eqs. (1) and (4) is surprising. This may only be a minor problem with the prefactors in the equations. Nevertheless, experiments in which the interactions between the substrates and the polymers can be

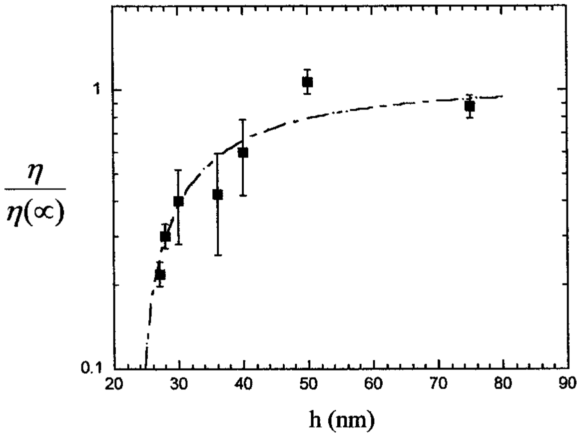

FIG. 4. The viscosity is shown to decrease appreciably with decreasing film thickness. The data were fit using Eq. (4) with constants, $\delta = 1.8$, $A = 3.2$ nm, and $K = 35$.

varied and further theory needs to be performed in order to resolve these and related issues.

Since both η and h are known, one might be tempted to use the WLF equation, or equivalently, the Vogel-Fulcher equation,

$$\ln\frac{\eta(T)}{\eta(T_g)}=\frac{c_1^g(T-T_g)}{c_2^g+(T-T_g)} \tag{4}$$

to calculate an effective viscosity for each film thickness. However, there are a number of complications that discourage this approach. The constants c_1 and c_2 in the WLF equation though largely empirical, are believed to constants, associated with the material [50]. These constants can also be defined in terms of the fractional free volume of the bulk material. In thin films, the packing of chain segments at a substrate will be different from those at the free surface and from those in the bulk. Moreover, the segmental mobility of chains at the free surface is higher than that at the substrate. Consequently, neither T_g, c_1, nor c_2 remain inherent "material" constants under these conditions, they depend on film thickness and on the substrate-polymer pair.

We now discuss possible effects of shear rate on the viscosities determined in this study. Some time ago, Dalnoki-Veress *et al.* examined the viscosities of freely standing films in the thickness range 100–400 nm by monitoring the growth of holes using optical microscopy [21]. They reported a decrease in mobility of the films and a strong shear-rate dependence of the magnitude of their measured viscosities. This shear-rate effect is not present in our system, as we show below. Graessley [51] proposed that the influence of shear rate might be evaluated by calculating a dimensionless strain rate parameter

$$\beta=\frac{\eta_0\overline{M}_w\dot{\gamma}}{\rho RT}. \tag{5}$$

In this equation η_0 is the zero shear viscosity, $\dot{\gamma}$ is the shear rate, ρ is the density, T is the temperature, R is the universal gas constant, and $\overline{M_w}$ is the weight average molecular weight. If $\beta<10$, then shear-rate effects are not important, and the viscosity is representative of a low shear-rate viscosity. We can calculate the shear rate in our experiments using the expression,

$$\dot{\gamma}=\frac{\sigma}{\eta}=\frac{S}{\eta h}. \tag{6}$$

This equation can be expressed in terms of the velocity of hole growth, $\dot{\gamma}=V_g/(bh)^{1/2}$ using $V_g=S/\eta(b/h)^{1/2}$ [27,32]. In our experiments, for an average velocity of $V_g=0.028\,37\ \mu\text{m/s}$ was determined for films of $h=40$ nm and an average $V_g=0.1006\ \mu\text{m/s}$ was determined for $h=27$ nm. The corresponding values of $\dot{\gamma}$ are $\dot{\gamma}_{40}=3.39\times10^{-2}$ and $\dot{\gamma}_{27}=0.146\ \text{s}^{-1}$, respectively. These values of $\dot{\gamma}$ enable us to determine typical values of β, using Eq. (6), in our experiment. With $M/(\rho RT)=3.48\times10^{-6}$ s/P for $\rho=1010\ \text{kg/m}^3$, $M=130$ kg/mol and $T=443$ K, $\beta(h=40)=4.92\times10^{-4}$ and $\beta(h=27)=2.12\times10^{-3}$ both of which are considerably less than 10. Therefore based on these calculations, there is no shear-rate effect on our estimates of the viscosities in our system. Dalnoki-Veress calculated values of β that were considerably larger than ours, ranging from ≈40–1500. Such large values are due largely to the fact that while their shear rates were comparable to ours, their experiments were conducted at 115 °C where their viscosities are many orders of magnitude larger than the viscosities in our study.

Our results can be addressed briefly in light of studies of chain dynamics near surfaces. Confinement can induce a slowing down of the dynamics [11]. In sufficiently thin films, the longest relaxation time τ_R of chains in thin layers can increase considerably over that of the bulk due to monomer-monomer interactions. This could lead to a larger effective viscosity, $\eta\propto\tau_R$ than in the bulk. In bulk systems, the reputation model predicts that the viscosity $\eta\propto N^3$ in the absence of monomer-monomer interactions. According to Semenov [9], when the layer thickness is less than the radius of gyration of the chain, segmental motions should be hindered by large potential barriers U due to monomer-monomer interactions in confined layers, so $\eta\propto N^3\exp(U)$. This effective barrier to chain motion is $U\propto h^{-2}$. These results clearly indicate that the viscosity should increase, or equivalently, the chain diffusion should slow down, in films that are sufficiently thin if $U>0$. It further suggests that near an interacting surface the dynamics should be slow. However, one must be cautioned that in our study, the dynamics are driven by an external driving force resulting in the lateral diffusion of the chains, on a noninteracting surface, $S<0$. In this regard the Semenov predictions cannot be directly compared with our experiments. Our results are more credibly rationalized in terms of the same phenomena that are responsible for changes in the apparent glass transition in the PS/SiO$_x$/Si system. The chain segments within a layer at the free surface have a much higher mobility than other chains in the system. Consequently, as the film becomes thinner, the effective mobility of the overall system increases, leading to a decrease in the viscosity with decreasing h.

CONCLUSION

In this paper we showed, using an indirect method, that the low-shear effective viscosity of entangled polystyrene thin films on SiO$_x$/Si substrates decreased appreciably with decreasing film thickness. The method is based on the fact that thin polymer films may rupture via the formation of holes that subsequently grow on the substrate. The large increase in the velocity of hole growth with decreasing h is consistent with a decreasing viscosity with decreasing film thickness for $25<h<50$ nm. This observation can be rationalized as follows. Since chain segments within a layer at the free surface have a much higher mobility than other chains in the system, then as the film becomes thinner, the effective mobility of the overall system increases, leading to a decrease in the viscosity with decreasing film thickness. In this regard, the same phenomena believed to be responsible for the apparent decrease of the glass transition with decreasing film thickness in this system also influences the viscosity. We note, however, that depending on the substrate polymer pair such trends are not expected to be general. If interactions between the polymer and substrate can be controlled systematically, then the variation of η with h, could be examined in further detail in other systems.

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[1] D. T. Wu, G. H. Fredrickson, J.-P. Creton, A. Ajdari, and L. Leibler, J. Polym. Sci., Polym. Phys. Ed. **33**, 2373 (1995).

[2] A. M. Mayes, Macromolecules **27**, 3114 (1994).

[3] W. Zhao, J. Sokolov, M. H. Rafailovich, R. J. Composto, S. D. Smith, M. Satowski, T. P. Russell, W. D. Dozier, and T. Mansfield, Macromolecules **26**, 561 (1993).

[4] J. L. Keddie, R. A. L. Jones, and R. A. Cory, Faraday Discuss. **98**, 219 (1994).

[5] S. D. Fryer, P. F. Nealey, and J. J. de Pablo, Macromolecules **33**, 6439 (2000).

[6] R. L. Jones, S. K. Kumar, D. L. Ho, R. M. Briber, and T. P. Russell, Nature (London) **400**, 146 (1999).

[7] W. E. Wallace, D. A. Fischer, K. Efimenko, W. L. Wu, and J. Genzer, Macromolecules **34**, 5081 (2001).

[8] P. G. deGennes, Eur. Phys. J. **2**, 201 (2000).

[9] A. N. Semenov, Phys. Rev. Lett. **80**, 1908 (1998).

[10] G. Reiter, Europhys. Lett. **23**, 579 (1993).

[11] G. Reiter, Macromolecules **27**, 3046 (1994).

[12] B. Frank, A. P. Gast, T. P. Russel, H. R. Brown, and C. Hawker, Macromolecules **29**, 6531 (1996).

[13] P. Calvert, Nature (London) **384**, 311 (1996).

[14] T. P. Russel and S. K. Kumar, Nature (London) **386**, 772 (1997).

[15] X. Zheng, B. B. Sauer, J. G. Van Alsten, S. A. Schwarz, M. H. Rafailovich, J. Sokolov, and M. Rubinstein, Phys. Rev. Lett. **74**, 407 (1995).

[16] X. Zheng, M. H. Rafailovich, J. Sokolov, Y. Strzhemechny, S. A. Schwarz, B. B. Sauer, and M. Rubinstein, Phys. Rev. Lett. **79**, 241 (1997).

[17] J. A. Torres, P. F. Nealey, and J. J. de Pablo, Phys. Rev. Lett. **85**, 322 (2000).

[18] E. K. Lin, W. Wu, and S. K. Satija, Macromolecules **30**, 7224 (1997).

[19] L. Xie, G. B. DeMaggio, W. E. Frieze, J. DeVries, D. W. Gidley, H. A. Hristov, and A. F. Yee, Phys. Rev. Lett. **74**, 4947 (1995).

[20] G. B. DeMaggio, W. E. Frieze, D. W. Gidley, M. Zhu, H. A. Hristov, and A. F. Yee, Phys. Rev. Lett. **78**, 1524 (1997).

[21] K. Dalnoki-Veress, B. G. Nickel, C. Roth, and J. R. Dutcher, Phys. Rev. E **59**, 2153 (1999).

[22] J. A. Forrest, K. Danolki-Veress, J. R. Stevens, and J. R. Dutcher, Phys. Rev. Lett. **77**, 2002 (1996).

[23] J. A. Forrest, K. Danolki-Veress, and J. R. Dutcher, Phys. Rev. E **56**, 5705 (1997).

[24] K. C. Tseng, N. J. Turro, and C. J. Durning, Phys. Rev. E **61**, 1800 (2000).

[25] G. F. Luengo, J. Schmitt, R. Hill, and J. Israelachvili, Macromolecules **30**, 2482 (1997).

[26] A. Vrij and J. Th. G. Overbeck, J. Am. Chem. Soc. **90**, 3074 (1968).

[27] F. Brochard-Wyart and J. Daillant, Can. J. Phys. **68**, 1084 (1991).

[28] H. S. Kheshgi and L. E. Scriven, Chem. Eng. Sci. **46**, 519 (1991).

[29] G. Reiter, Phys. Rev. Lett. **68**, 75 (1992).

[30] G. Reiter, Langmuir **9**, 1344 (1993).

[31] T. G. Stange, D. F. Evans, and W. A. Hendrickson, Langmuir **13**, 4459 (1997).

[32] F. Brochard-Wyart, G. Debrégeas, R. Fondecave, and P. Martin, Macromolecules **30**, 1211 (1997).

[33] R. Xie, A. Karim, J. F. Douglas, C. C. Han, and R. A. Weiss, Phys. Rev. Lett. **81**, 1251 (1998).

[34] A. Sharma and R. Khanna, Phys. Rev. Lett. **81**, 3463 (1998).

[35] K. Jacobs, S. Herminghaus, and K. R. Mecke, Langmuir **14**, 965 (1998).

[36] R. Segalman and P. F. Green, Macromolecules **32**, 801 (1999).

[37] R. Limary and P. F. Green, Langmuir **15**, 5617 (1999).

[38] J.-L. Masson and P. F. Green, J. Chem. Phys. **112**, 349 (2000).

[39] J. C. Meredith, A. P. Smith, A. Karim, and E. J. Amis, Macromolecules **33**, 9747 (2000).

[40] J. L. Masson, R. Limary, and P. F. Green, J. Chem. Phys. **114**, 10 963 (2001).

[41] R. Seeman, S. Herminghaus, and K. Jacobs, Phys. Rev. Lett. **86**, 5534 (2001).

[42] U. Thiele, M. G. Velarde, and K. Neuffer, Phys. Rev. Lett. **87**, 016104 (2001).

[43] I. Karapanagiotis, W. W. Gerberich, and D. F. Evans, Langmuir **17**, 2375 (2001).

[44] I. Karapanagiotis, D. F. Evans, and W. W. Gerberich, Langmuir **17**, 3266 (2001).

[45] A. Sharma and A. T. Jameel, J. Colloid Interface Sci. **161**, 190 (1993).

[46] A. J. De Vries, Recl. Trav. Chim. Pays-Bas. **77**, 383 (1958).

[47] J.-L. Masson, O. Olufokunbi, and P. F. Green (unpublished).

[48] P. G. de Gennes, Rev. Mod. Phys. **57**, 827 (1985).

[49] W. W. Graessley and J. Roovers, Macromolecules **12**, 959 (1979).

[50] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980).

[51] W. W. Graessley, Adv. Polym. Sci. **16**, 1 (1974).

[52] C. Redon, F. Brochard-Wyart, and F. Rondelez, Phys. Rev. Lett. **66**, 715 (1991).

[53] K. R. Shull and T. E. Karis, Langmuir **10**, 334 (1994).