

Crystal Growth Rate in Ultrathin Films of Poly(ethylene oxide)

K. DALNOKI-VERESS,¹ J. A. FORREST,² M. V. MASSA,¹ A. PRATT,³ A. WILLIAMS³

¹Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4M1, Canada

²Department of Physics and Guelph-Waterloo Physics Institute, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

³Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, United Kingdom

Received 8 May 2001; revised 1 August 2001; accepted 1 August 2001

ABSTRACT: Many dynamical properties of polymers, including segmental relaxation and chain diffusion, exhibit anomalies in thin-film samples. We extend the studies of thin-film dynamics to the case of semicrystalline polymers and present a study of the crystal growth rate for thin films of poly(ethylene oxide). We used optical microscopy and quartz crystal microbalance techniques to characterize the kinetics of crystallization for films with thicknesses from 40 to 1000 nm for a range of temperatures near the melting point. A remarkable slowing down of the crystal growth is observed at all temperatures studied for films with a thickness of less than ~ 100 nm. The results can be used to suggest reductions of the mobility of chains at the crystal/amorphous interface. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part B: Polym Phys* 39: 2615–2621, 2001
Keywords: crystallization; thin films; poly(ethylene oxide); chain mobility; spherulites

INTRODUCTION

Polymer crystallinity in confinement is of tremendous interest especially because of the expectation that these studies can in some way elucidate fundamental issues of polymer crystallization in general. However, we must realize that because a significant fraction of industrially relevant polymers are semicrystalline, understanding of crystallinity in thin films and at interfaces is of paramount importance. There are various approaches to confining semicrystalline polymers with the general consensus that the crystallization kinetics and morphology are affected. For

example, the diverse phases of block copolymers,^{1–6} confinement in pores,⁷ and the thin-film geometry^{8–19} all provide evidence that the kinetics and morphology of semicrystalline polymers are significantly affected. There are several length scales below which confinement might be expected to affect crystallization. We would expect that the kinetics of crystallization are affected when the confinement results in changes in the glass-transition temperature (T_g), which for polystyrene films on a substrate occurs at ~ 50 nm.²⁰ Reductions in T_g have also been linked to the end-to-end size of a polymer molecule²¹: a length scale below which the kinetics of crystallization might also be affected. Likewise, when the confining dimensions start to approach the length scale of the lamellar thickness of the polymer crystals, d , anomalous behavior may be expected.

The multitude of block copolymer mesophases provide a tremendous opportunity for studying con-

Contribution from the March 2001 Meeting of the American Physical Society—Division of Polymer Physics, Seattle, WA
Correspondence to: K. Dalnoki-Veress (E-mail: dalnoki@mcmaster.ca)

Journal of Polymer Science: Part B: Polymer Physics, Vol. 39, 2615–2621 (2001)
© 2001 John Wiley & Sons, Inc.

finement in one-dimension (lamellae), two-dimensions (cylinders), and three-dimensions (spheres) at very small length scales (~ 10 nm). The first of these studies were carried out by Lotz and Kovacs¹ on poly(ethylene oxide)-*block*-polystyrene diblocks (PEO-*b*-PS). The same PEO-*b*-PS system has been studied in great detail by Cheng's group.^{2,3} For example, Zhu and coworkers^{2,3} investigated crystallization in a lamellar phase of PEO-*b*-PS where they observed changes from bulk behavior in the kinetic effects as well as carrying out detailed measurements of the orientation of the crystal axis within the lamellae. Loo, Register and Ryan⁴ have applied time-resolved X-ray scattering to probe the dynamics of crystallization in 25-nm spherical mesophases of a polyethylene block connected to a random styrene-ethylene-butene terpolymer block. The study revealed that the isothermal crystallization kinetics of the confined system was affected by comparison to a bulk system, as was the degree of undercooling required to crystallize the samples. In a similar study, Loo et al.⁵ were able to image the microdomain and crystallite morphologies of a poly(ethylene-*block*-vinylcyclohexane) and study the configuration of the crystallites within these domains. Surprisingly, a study of thin films of a PEO-*b*-polybutadiene (PEO-*b*-PB) diblock by Hong et al.⁶ resulted in the observation that adjacent layers of the crystallites were in orientational registry while separated by ~ 10 -nm layers of the PB block. The orientational correlation between adjacent layers must be the result of a common nucleus, and it was proposed by Hong et al.⁶ that this is achieved through edge and screw dislocations in the microphase structure.

A different approach was taken by Filippov, Doroginikij and Vartapetyan⁷ who confined PEO in cylindrical pores of active carbon with an average diameter of 48 nm. The kinetics of crystallization was studied in these samples by looking at the induction period and found to be a factor of two longer for PEO confined to pores as compared with the bulk.

The use of ultrathin films to study one-dimensional confinement provides a very simple and versatile method by which the confinement effects on crystallization can be examined. In a series of seminal articles by Frank, Despotopoulou and coworkers,⁸⁻¹⁰ poly(di-*n*-hexyl silane) films as thin as ~ 10 nm were studied. Specifically they observed the following: (1) the final degree of crystallinity decreased with decreasing film thickness, h , while being almost insensitive to the substrates used; (2) crystallization occurs faster for

thicker films than for thinner films and was completely inhibited in the thinnest films (~ 15 nm); and (3) these results were observed both for high and low molecular weight polymers indicating that chain dimension and entanglement cannot account for these observations. Kressler, Wang and Kammer¹¹ investigated poly(ϵ -caprolactone) films in which dewetting of the polymer could be made to take place at the same time as crystallization with surprising morphologies as a result of the two competing phenomena. A real-time atomic force microscopy (AFM) study by Pearce and Vancso¹² focused on both melting and crystallization of PEO. In this study, the same lateral crystal-growth rate was obtained at small length scales (AFM) and at large length scales (optical microscopy). In addition, the researchers directly observed a depletion zone of amorphous material at the melt/crystal interface. AFM was also used by Reiter and Sommer¹³⁻¹⁵ to explore crystallization in PEO monolayers adsorbed onto the oxide layer on Si substrates. Perhaps the most important aspect of this work is that, in contrast to the work by Frank et al.⁸, they observed crystallization at monolayer length scales. In this system the area occupied by an adsorbed monolayer is greater than the area required by the crystalline phase, resulting in a limited diffusion of the adsorbed chains to the crystal front. This diffusion limited aggregation process results in a fingering instability. The associated morphologies and width of the fingers were explained in terms of a simple model and computer simulations. A very novel system was studied by Prud'homme's group:¹⁶ films of a miscible blend of poly(ϵ -caprolactone) (PCL) and poly(vinyl chloride) in which the PCL component crystallizes. They found that a surface enrichment of PCL results in dramatic changes in the growth rate of crystals depending on the distance of a nucleation site from the enriched interface.

The main objective of this article is to examine the crystal growth rate under isothermal crystallization conditions in thin films. Other researchers have recently performed a similar study on isotactic polystyrene (is-PS) films with film thicknesses as low as 25 nm.^{17,18} The results obtained show that the thinnest films have growth rates, G , that are about 75% of the saturation value for thick films. An analysis of the data by fitting to $G(h) = G(\infty)(1 - d/h)$ results in a constant value for $d = 6$ nm, independent of the crystallization temperature, T_c , the weight-average molecular weight M_w , and the substrate used. Work from

the same group found that the morphology of the crystals was also affected.¹⁹

In this article, we measure the growth rate of spherulitic crystals of PEO films with optical microscopy for films as thin as 40 nm (the use of the term 'spherulite' is somewhat misleading because within the film the 'spherulite' grows laterally in two dimensions and is constrained in the film's normal direction, i.e., a crystalline disk). The studies that were performed for various film thicknesses, crystallization temperatures, and on two substrates reveal a reduction in G from the bulk value. Remarkably this reduction in G corresponds to a factor of three decrease for the thinnest film when compared with bulk values and is independent of the substrates used. The data analysis indicates that it is the chain-transport mechanism that is affected by the confinement rather than the energy barrier associated with nucleating chains at the crystal front. A quartz crystal microbalance technique is also used to examine the kinetics of crystallinity and proves to be a valuable tool for further studies of crystallinity in very thin films.

EXPERIMENTAL

High molecular weight ($M_w = 272,000$), monodisperse ($M_w/M_n = 1.14$) PEO (Polymer Source Inc., Dorval Quebec, Canada) was dissolved in acetonitrile with polymer mass fractions ranging from 0.65 to 3.00%. The solutions were spin coated onto three of the following types of substrates: (1) Si with the native oxide layer present, (2) Si substrates onto which a 110-nm layer gold was evaporated, and (3) the gold electrode on the quartz crystals used in the QCM measurements. This study focused on film thicknesses ranging from 40 to 1000 nm as measured by ellipsometry and AFM. The QCM crystal was placed in a temperature-controlled sample environment, and absolute temperatures were measured to within 0.5 °C. For the optical microscopy measurements a commercial hot stage (Linkam THMS-600) controlled the sample temperature to within the same tolerance. The bulk of the measurements were carried out in air although data were also obtained in argon as well as nitrogen to rule out effects as a result of humidity and oxygen.

Both QCM and video optical microscopy were used for the study of crystallization in the thin PEO films. The QCM is a very sensitive ultrasonic technique where, in this novel implementation

developed by Q-sense,²³ the crystal with gold electrodes is driven at resonance (~ 10 MHz) and then disengaged from the driving circuit. The decaying oscillation is measured with an oscilloscope, and both the resonant frequency and the decay envelope of the voltage signal are fit to the functional form, $V(t) = \exp(-t/\tau)\cos(2\pi ft)$, where t is time, τ defines the decay envelope, and f is the frequency of oscillation. The energy dissipation per cycle, D (also known as the inverse of the Q-factor), of the crystal/sample system is given by $D = (2\pi f\tau)^{-1}$ and depends on the shear loss in the system. For the study of crystallization, the dissipation factor provides valuable information. The shear loss modulus of the crystalline and liquid phases are very different, and hence the change in the dissipation is simply proportional to the area of the film on the active area of the quartz crystal that remains liquid: $\Delta D \sim A(\text{liq})$. The QCM used in this manner is very sensitive to the crystallinity of the sample, with the ability to track the crystal volume fraction in films as thin as tens of nanometers. This is only possible because of the tremendous sensitivity provided by the Q-sense instrument. In this study, we focus on the isothermal crystal-growth rate and unfortunately although the QCM is a very sensitive tool, the crystal-growth rate cannot be determined independently. This is because the QCM measurement of the dissipation depends not only on the crystal-growth rate but also on the number of crystals on the active area.

Video optical microscopy provides a very straightforward approach to probing the growth rate of crystals provided the boundary between the crystal and the liquid can be visualized and followed as a function of time. Dark field microscopy provided the most contrast. In this mode, the sample is illuminated off-normal to the sample surface, and most of the light seen through the microscope is scattered by the crystals. This gives the appearance of white crystals in a black background as seen in Figure 1. The only drawback of this optical method is that it was found to be limited to films with a thickness, h , greater than ~ 40 nm as a result of the lack of contrast.

RESULTS AND DISCUSSIONS

Although the QCM technique was not used for the bulk of the data on which this article is based, the technique did prove to be very sensitive and provided complimentary information. In Figure 2 we



Figure 1. Optical micrographs of a 200-nm PEO film. The time interval between images is 20 s, and each image is 620 μm wide. The sample is crystallized isothermally at 48 $^{\circ}\text{C}$.

show the dissipation, D , for a 200-nm film as a function of time for five different isothermal crystallization experiments. For these measurements the samples were annealed for 20 min at 80 $^{\circ}\text{C}$, a temperature above the ideal melting temperature, $T_m = 68$ $^{\circ}\text{C}$, followed by a rapid quench to the crystallization temperature, T_c . We clearly see the expected behavior: initially there is no change in the dissipation during the induction period until nuclei are formed at which point D decreases as a result of the growth of the spherulites; after some time the spherulites impinge on each other, and the rate of change of crystallinity slows down. For higher degrees of undercooling the process is observed to occur much faster because the driving force to crystallize is larger (when the crystallization temperature is changed from 54 to 50 $^{\circ}\text{C}$ almost an order of magnitude change in the timescale is seen).

In the second type of experiment, the sample was cooled at some specified ramp rate until the sample had fully crystallized and then heated again at the same rate. Figure 3 depicts the re-

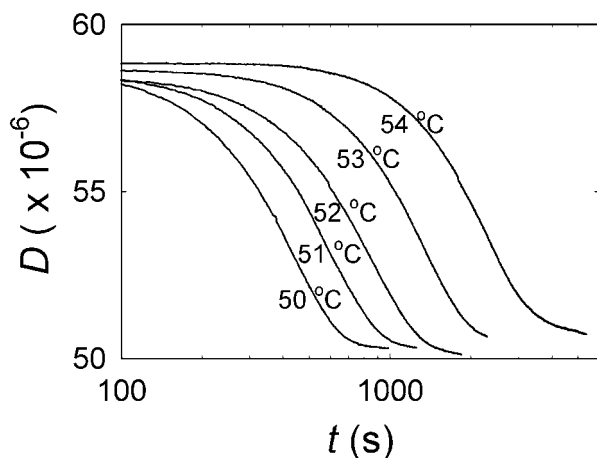


Figure 2. QCM measurement of the dissipation factor as a function of time for a film thickness of 200 nm and five isothermal crystallization temperatures.

sults of such an experiment for four different ramp rates ranging from 10 to 1 $^{\circ}\text{C}/\text{min}$. For the faster ramp rates, the liquid can be supercooled further before the sample crystallizes. Upon heating the temperature at which the crystals melt is found to be the same. The ease of using the QCM to carry out such measurements for even very thin films makes this an ideal tool for the study of crystallinity in confined systems.

This article focuses on the crystal-growth rate rather than the more complicated issue of crystallinity in confinement which is dependent on both the crystal-growth rate and the nucleation rate of new crystals and may also be affected by confinement.⁷ Optical microscopy studies, as shown in Figure 1, can be used to obtain the radius of the spherulite as a function of time and hence the growth rate, G . In Figure 4 we plot the change in the radius as a function of time for a 200-nm film. For these isothermal crystallization experiments, the samples were annealed at 80 $^{\circ}\text{C}$ for 20 min before quenching to the crystallization temperature $T_c < T_m$. The results for six different values of T_c are illustrated in Figure 4, and in

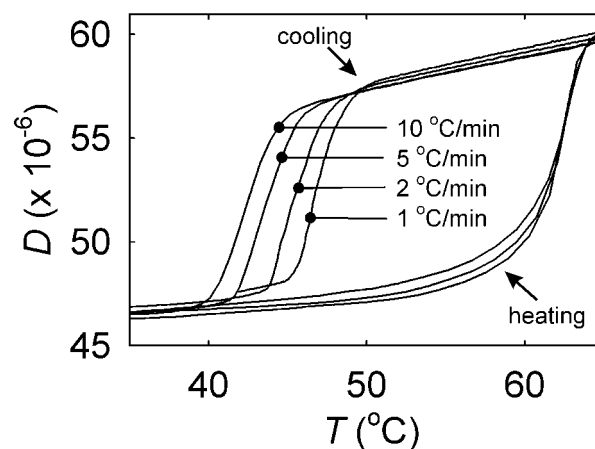


Figure 3. The QCM dissipation factor as a function of temperature for four different temperature ramp rates for a 200-nm film.

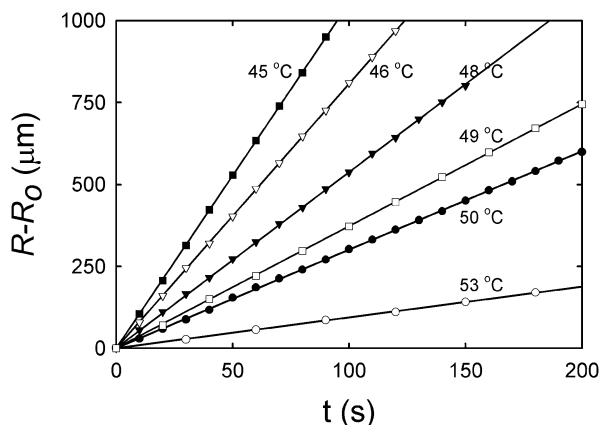


Figure 4. The change in the radius as a function of time for six different isothermal crystallization temperatures, $h = 200$ nm.

each case we obtain a best fit value of the slope G . As with the QCM results, we see the expected behavior, that is, an increase of G with an increase in the degree of supercooling. In this way the growth rate was obtained for nine film thicknesses ($40 \text{ nm} < h < 1000 \text{ nm}$) and at least seven crystallization temperatures for each film thickness ranging from 42 to 56 °C. The results for six film thicknesses are represented in Figure 5 where we plot the growth rate as a function of the T_c . A surprising result is immediately obvious: decreases in the film thickness result in reductions in the growth rate. Similar results have been observed previously in studies of isotactic polystyrene.^{17,18} The decrease in G is significant and corresponds to approximately a factor of

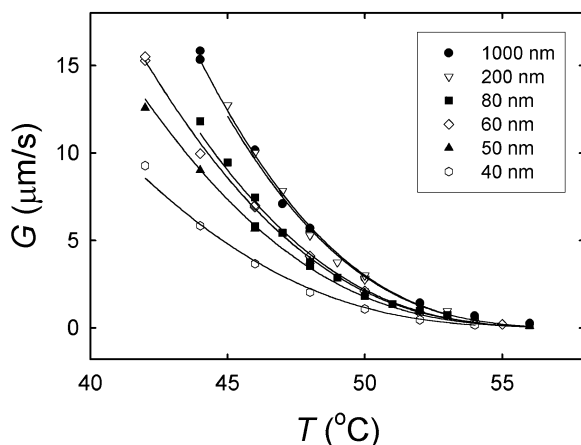


Figure 5. The growth rates obtained for six film thicknesses at various isothermal crystallization temperatures.

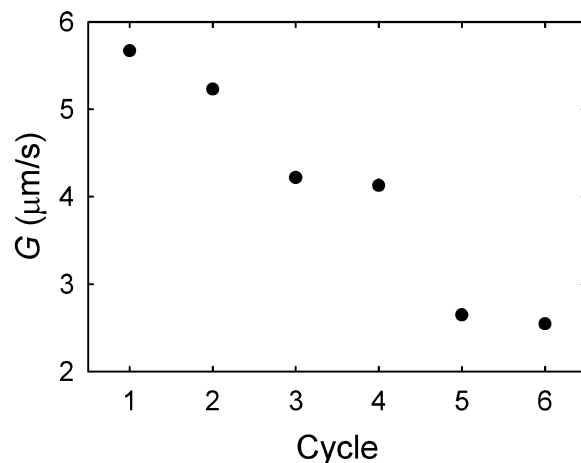


Figure 6. Growth rate in subsequent cycles on the same sample. Isothermal crystallization at 46 °C, $h = 50$ nm.

three difference between the two thickness extremes (as compare with isotactic polystyrene where the growth rate was found to be ~ 0.75 of the bulk value for similar thickness values¹⁷).

A technical difficulty observed with these measurements was systematic changes in the sample upon thermal cycling. Initially many crystallization runs were performed on the same sample by reannealing at 80 °C for 10 min. It was found that under identical conditions the growth rate decreased in subsequent cycles (see Fig. 6).²⁴ Currently we do not fully understand this result, although preliminary studies indicate that this is due to surface roughness of the melt that is not fully annealed away before recrystallizing the sample. This claim is consistent with the observation that longer annealing times between cycles diminished the reduction in the growth rate. To avoid this problem we used only first-cycle data as well as longer annealing times (20 min). With these precautions, reproducible data could be obtained that were independent of the atmosphere in which the experiments were carried out (air, nitrogen, and argon). All the data used in the following analysis and shown in the figures are obtained in this way.

We now return to the results of Figure 5. To fully characterize these results, the expression for the temperature dependence of the crystal-growth rate can be used

$$G \sim \exp[-\Delta F^*/kT] \exp[-\Delta G^*/kT];$$

where ΔF^* is the activation barrier to chain transport, and ΔG^* is the free-energy barrier for nucle-

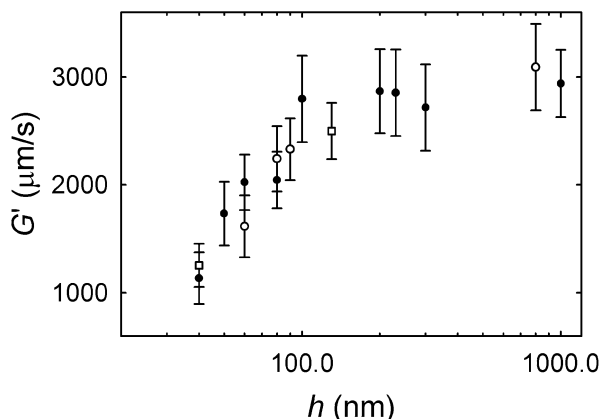


Figure 7. Temperature-independent growth rate (see text for definition) as a function of the film thickness. The solid circles are the data for PEO films on a Si substrate with the native oxide layer present, whereas the open squares are for measurements carried out entirely in an Ar atmosphere. The open circles are for measurements of the growth rate of PEO on a Au substrate.

ation.^{25,26} For a small temperature range close to T_m we can ignore the temperature dependence of the activation barrier to chain transport (i.e., over a small temperature range at $T \gg T_g$, chain mobility is constant with T), and using²⁵ $\Delta G^* \sim 1/(T_m - T)$ we rewrite the crystal-growth rate as

$$G = G' \exp[-b/T(T_m - T)].$$

This expression has the important characteristic that the crystal-growth parameter G' is *independent of the temperature* (for the small temperature range studied) and describes chain transport, whereas b is a parameter that characterizes the energy barrier to the nucleation of a new polymer segment at the crystal surface. Remarkably, the data for all film thicknesses can be fit very well using this expression with a *single value of b* , whereas the crystal-growth parameter $G'(h)$ is film-thickness dependent (see solid lines in Fig. 5). In the data analysis we used $T_m = 68$ °C and obtained a best fit value for $b = (4.0 \pm 0.3) \times 10^4$ K². The best fit value of b was fixed for the fits to obtain the values of $G'(h)$ plotted in Figure 7. The figure illustrates unambiguously the factor of three decrease in the crystal-growth rate for the thinnest film for the entire temperature range studied. The excellent fit to the data obtained with a single value of b indicates that the energy barrier to the nucleation of a new polymer segment at the crystal surface is unaffected by the

confinement for the film thicknesses studied (i.e., the drive to crystallizing is not dependent on h for the range of h studied). In contrast to b , the growth parameter $G'(h)$ is strongly film-thickness dependent and is indicative of anomalous chain transport at the crystal/amorphous interface in the thin PEO films. A somewhat different analysis of the data obtained for isotactic polystyrene, it-PS, resulted in similar claims by Sawamura et al.¹⁷ To verify if the observed behavior was the result of some substrate interaction, the measurements were repeated on a gold substrate with identical results as shown in Figure 7. In addition, measurements of the crystal-growth rate on Si substrates annealed and crystallized in argon are also shown in Figure 7. Within the experimental uncertainty, the data obtained for all measurements are consistent regardless of the substrates used and the atmosphere (air, nitrogen, and argon) in which the experiments were carried out.

The simple analysis of the data implies that it is the chain transport that is affected. Unfortunately it is not possible for us to provide a mechanism responsible for the anomalous chain transport. For studies of the T_g of polystyrene, both on substrates and in a free-standing geometry reduction of T_g with decreasing film thickness was observed. This seems to oppose the inhibited chain transport for thin films observed in this PEO study as well as similar results obtained by Sawamura et al.¹⁷ for it-PS. However, these observations should not be taken as contradictory because the segmental mobility probed in a T_g experiment and the chain mobility associated with a chain attaching itself to a crystal surface are vastly different.

SUMMARY

In this article, we report on the kinetics of crystallinity in thin films of PEO. A QCM technique was used to track the crystallinity in films that are only tens of nanometers thick. Using the QCM it was possible to track the kinetics of crystallinity in isothermal experiments as well as the degree of supercooling with various temperature ramp rates. Optical microscopy was used to observe reductions in the growth rate of spherulites when confined to a thin-film geometry. As the film thickness was reduced from 1000 to 200 nm, no change in the crystal-growth rate, G , could be measured; however, further decreases in the film

thickness to 40 nm caused a factor of three decrease in G . This result was observed over temperatures ranging from 42 to 56 °C and found to be independent of the substrate interaction for the two substrates studied as well as independent of the atmosphere in which the experiments were carried out. Although a cause for the reductions in G could not be provided on the basis of the current data, a simple analysis indicates that it is the chain transport that is affected by the confinement and not the energy barrier associated with nucleating additional chain segments at the crystal front.

The authors thank Profs. S. Z. D. Cheng, R. A. L. Jones, Y. Miyamoto, and R. E. Prud'homme for the helpful discussions. This work was funded in part by EPSRC of the U.K. and NSERC of Canada.

REFERENCES AND NOTES

- Lotz, B.; Kovacs, A. J. *Kolloid Z Z Polym* 1966, 209, 97.
- Zhu, L.; Cheng, S. Z. D.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Hsiao, B. S.; Yeh, F.; Lotz, B. *Polymer* 2001, 42, 5829.
- Zhu, L.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Cheng, S. Z. D.; Thomas, E. L.; Hsiao, B. S.; Yeh, F.; Liu, L.; Lotz, B. *Macromolecules* 2001, 34, 1244.
- Loo, Y.-L.; Register, R. A.; Ryan, A. J. *Phys Rev Lett* 2000, 84, 4120.
- Loo, Y.-L.; Register, R. A.; Adamson, D. H. *J Polym Sci Part B: Polym Phys* 2000, 38, 2564.
- Hong, S.; MacKnight, W. J.; Russell, T. P.; Gido, S. P. *Macromolecules* 2001, 34, 2883.
- Filippov, A. V.; Doringizkij, M. M.; Vartapetyan, R. Sh. *Magn Reson Imaging* 1998, 16, 631.
- Frank, C. W.; Rao, V.; Despotopoulou, M. M.; Pease, R. F. W.; Hinsberg, W. D.; Miller, R. D.; Rabolt, J. F. *Science* 1996, 273, 912.
- Despotopoulou, M. M.; Frank, C. W.; Miller, R. D.; Rabolt, J. F. *Macromolecules* 1996, 29, 5797.
- Despotopoulou, M. M.; Miller, R. D.; Rabolt, J. F.; Frank, C. W. *J Polym Sci Part B: Polym Phys* 1996, 34, 2335.
- Kressler, J.; Wang, C.; Kammer, H. W. *Langmuir* 1997, 13, 4407.
- Pearce, R.; Vancso, G. J. *Macromolecules* 1997, 30, 5843.
- Reiter, G.; Sommer, J.-U. *Phys Rev Lett* 1998, 80, 3771.
- Reiter, G.; Sommer, J.-U. *J Chem Phys* 2000, 112, 4376.
- Sommer, J.-U.; Reiter, G. *J Chem Phys* 2000, 112, 4384.
- Prud'homme, R. E. Private communication and Mareau, V. M.S. Thesis, Laval University, Guelph, Ontario, 2000.
- Sawamura, S.; Miyaji, H.; Izumi, K.; Sutton, S. J.; Miyamoto, Y. *J Phys Soc Jpn* 1998, 67, 3338.
- Izumi, K.; Ping, G.; Hashimoto, M.; Toda, A.; Miyaji, H.; Miyamoto, Y.; Nakagawa, Y. In *Advances in the Understanding of Crystal Growth Mechanisms*; Nishinaga, T.; Nishioka, K.; Harada, J.; Sasaki, A.; Takei, H., Eds.; Elsevier Science: Amsterdam, 1997; p 337.
- Taguchi, K.; Miyaji, H.; Izumi, K.; Hoshino, A.; Miyamoto, Y.; Kokawa, R. *Polymer* 2001, 42, 7443.
- Forrest, J. A.; Dalnoki-Veress, K. *Adv Colloid Interface Sci*, in press, 2000.
- Dalnoki-Veress, K.; Forrest, J. A.; Murray, C.; Gigault, C.; Dutcher, J. R. *Phys Rev E: Stat Phys Plasmas Fluids Relat Interdiscip Top* 2001, 63, 031801.
- Q-Sense AB, Göteborg, Sweden.
- Miyamoto, Y., Kyoto University. Private email communication: similar issues associated with changes in the growth rate of for PEO films have been observed in Prof. Miyaji's group of Kyoto University.
- Magill, J. H. In *Polymer Handbook*, 3rd ed.; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1982, pp VI 1279–VI 1286.
- Strobl, G. *The Physics of Polymers: Concepts for Understanding Their Structures and Behavior*, 2nd ed.; Springer-Verlag: Berlin, 1997, pp 143–190.