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Direct Measurement of Molecular Motion in Freestanding Polystyrene Thin Films

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S *Supporting Information*

ABSTRACT: An optical photobleaching technique has been used to measure the reorientation of dilute probes in freestanding polystyrene films as thin as 14 nm. Temperature-ramping and isothermal anisotropy measurements reveal the existence of two subsets of probe molecules with different dynamics. While the slow subset shows bulk-like dynamics, the more mobile subset reorients within a few hundred seconds even at $T_{g,DSC} - 25$ K ($T_{g,DSC}$ is the glass transition temperature of bulk polystyrene). At $T_{g,DSC} - 5$ K, the mobility of these two subsets differs by 4 orders of magnitude. These data are interpreted as indicating the presence of a high-mobility layer at the film surface whose thickness is independent of polymer molecular weight and total film thickness. The thickness of the mobile surface layer increases with temperature and equals 7 nm at $T_{g,DSC}$.

In many applications of thin polymer films, the mobility of small molecules and the segmental dynamics of the polymer itself are important. For electronic devices including batteries, the mobility of small molecules that carry charge can play a crucial role. For sensors, mobility is often required to allow access for the target molecule or to allow molecular rearrangements following a triggering event. The segmental dynamics that control the mobility of small molecules also determines important mechanical properties of the polymer film. As device miniaturization is often required to enhance performance, considerable attention has been given to changes in the properties of polymeric systems as they are reduced to the nanometer length scale. For such systems, most of the sample is near an interface, and thus understanding how the interface influences the mobility of small molecules and the polymer itself is of importance.

Freestanding polymer films are ideal for investigating the influence of nanoscale dimensions since complexities due to polymer−substrate interactions need not be considered. To date, most studies of freestanding polymer films have focused on measuring the glass transition temperature T_g by directly or indirectly probing density changes with temperature.[1−6] For bulk polymers, it is well-established that T_g measured in this way correlates well with the mobility of small molecules in the polymer and the mechanical properties of the polymer itself. However, existing work suggests that this correlation is significantly altered in thin films, and thus measurement of T_g based upon density changes may not provide accurate information about molecular mobility for thin-film applications. For example, the segmental relaxation times inferred from the T_g values of thin polymer films cannot be easily reconciled with measurements of the terminal dynamics probed by hole formation and growth.[7−9] If T_g measurements cannot provide accurate predictions of physical properties relevant for applications, direct measurements of the molecular mobility in thin films are required. Only a few studies of freestanding polymer films have investigated segmental dynamics, including a nanobubble inflation study[10] and dielectric relaxation studies.[11,12] The former is an indirect measurement of dynamics, and the latter presented limited results. Recent work[13] indicates that dynamics near a free polymer surface can be significantly enhanced, and it is widely recognized that understanding the spatial distribution of mobility in freestanding[12] and supported films[14] is an important goal.

Here we present the first quantitative characterization of the spatial variation of molecular mobility within thin freestanding polymer films. We measure the reorientation of dilute probe molecules in films as thin as 14 nm. We find two subsets of probe molecules with distinct dynamics. While some of the probes show bulk-like dynamics, another group is much faster, by a factor of ~10^4 at 5 K below the bulk T_g. Contributions from both subsets were seen for film thicknesses from 14 to 47 nm. These data are interpreted as indicating the presence of a high-mobility layer at the film surface whose thickness is independent of polymer molecular weight and total film thickness. The thickness of the mobile surface layer increases with temperature and equals 7 nm at the bulk T_g. As there is a strong correlation between probe reorientation and segmental dynamics in bulk polymers,[15−18] we expect that the segmental dynamics at the surface of a freestanding film is much faster than in the interior. At a minimum, the present study definitively establishes the mobility of small molecules in thin polymer films.

A photobleaching technique[15,19−21] was used to study the reorientation of probe molecules in freestanding polystyrene films.[18] A trace amount of fluorescent probe (~1 ppm) was dispersed in the polymer film, and a pattern was photobleached using linearly polarized light. As a result, anisotropy was created in the orientation of the transition dipole moments of the unbleached probes. Less intense circularly polarized light was used to monitor the fluorescence intensities parallel and perpendicular to the bleaching beam, and the anisotropy was calculated using these intensities. The anisotropy decay was measured both isothermally and during temperature ramping.[18]

Polystyrenes with molecular weights 160, 984, and 7370 kg/mol were used in this study. The fluorescence probes were *N*,*N*′-bis(2,5-di-*tert*-butylphenyl)3,4,9,10perylenedicarboximide

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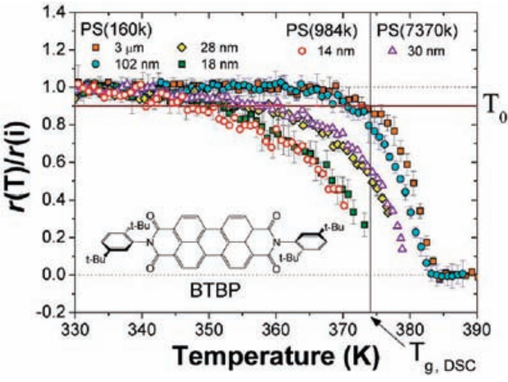

Figure 1. Temperature-ramping anisotropy measurements of the probe molecule BTBP (stucture shown as inset) in freestanding polystyrene films of various thicknesses and molecular weights.

(BTBP; structure in Figure 1) and 4,4-difluoro-5,7-diphenyl-4-bora-3a,4a-diaza-*s*-indacene-3-dodecanoic acid (Bodipy C12; structure in Supporting Information (SI)). Thin films (<100 nm) were spin-coated onto freshly cleaved mica from a solution of polymer and probe. Freestanding films were prepared by floating the film onto water and transferring to a copper TEM grid. Samples were annealed in a vacuum oven (0.1 Torr) before ($T_{g,DSC}$ + 20 K, 12 h) and after (~$T_{g,DSC}$, 12 h) transfer to the copper grid. Anisotropy measurements were carried out with a confocal fluorescence microscope with the sample in a dewar that controlled both temperature and pressure. Other details of the experimental apparatus and the data analysis are provided in the SI.

Figure 1 presents temperature-ramping anisotropy measurements for the probe BTBP in freestanding polystyrene films ranging from 3 μm to 14 nm in thickness. For these measurements, a pattern was photobleached at low temperature, and the temperature was ramped at 2 K/min. The 3 μm film shows bulk dynamics; the anisotropy is constant and then drops rapidly to zero near $T_{g,DSC}$.[18] This result is consistent with the physical picture of the probe being "trapped" in the polymer at low temperatures and losing anisotropy only when the segmental dynamics of polymer allow the probe to rotate. For thinner films, the anisotropy decay initiates at lower temperature and occurs over a wider temperature range. These scans were terminated at the highest temperature that avoided hole formation in the film. Most data in Figure 1 were obtained on polystyrene films with M_n = 160 kg/mol. For the higher molecular weight films, only a single anisotropy decay is shown (14 nm for 984 kg/mol and 30 nm for 7370 kg/mol). Clearly there is no discernible molecular weight dependence (see additional data in Figure S2 in the SI). As shown in the SI, we verified that no anisotropy decay occurs at temperatures below 330 K, and thus the temperature range shown in the main part of Figure 1 captures all the dynamics relevant for probe reorientation.

Although it is clear from Figure 1 that the probes rotate faster in thinner films, it is misleading to define a single temperature shift to describe the effect of film thickness since the shape of the anisotropy decay changes. Nevertheless, for ease of comparison with the literature, we define a temperature $T_{0.9}$ where the normalized anisotropy drops to 0.9. By this measure, a 28 K shift is observed for the 14 nm film relative to the bulk. A comparison with literature values of T_g shifts for thin polystyrene films is provided in the Figure 2S in the SI. It is notable that $T_{0.9}$ is independent of molecular weight, whereas T_g for freestanding polystyrene thin films has been reported to depend strongly on molecular weight.[2-4] This comparison emphasizes that, in contrast to bulk systems, molecular mobility in thin films cannot be predicted from T_g measurements.

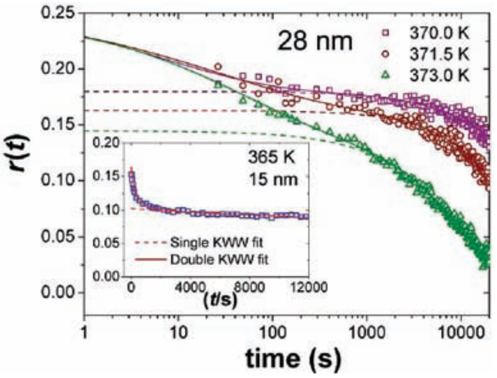

Figure 2. Isothermal anisotropy decays for BTBP in a 28 nm freestanding PS(160k) film at the temperatures indicated. The solid and dotted lines are fits to double and single KWW functions, respectively. Inset: Data for a 15 nm film at 365 K with a linear time axis. Clear evidence is observed for the existence of a fast subset of probe molecules.

Isothermal anisotropy measurements of thin freestanding polystyrene films show clear evidence for a fast decay process which is not observed in thick polymer films. Unlike isothermal anisotropy measurements on thick polystyrene films (Figure 1S in SI), the thin-film data shown in Figure 2 cannot be fitted to a single stretched exponential [Kohlrausch−Williams−Watts (KWW)] function. Figure 2 shows data for a 28 nm film at three temperatures; in each case, a fast decay is observed. This effect is even more apparent in thinner films, as shown in the inset for a 15 nm sample. The thin-film data are well-described by a function of two additive KWW functions (solid lines), as described in the SI.

The two-stage anisotropy decays shown in Figure 2 suggest the existence of two subsets of probe molecules that exhibit substantially different dynamics. A detailed analysis of the decay curves strongly supports this view. Figure 3 shows relaxation times for the fast (yellow circles) and slow (red triangles) processes observed in thin films as obtained from the double KWW fits. These relaxation times were obtained from isothermal experiments on films in the range of 18−28 nm and show no apparent dependence on film thickness. Also shown in Figure 3 are the reorientation times (*) for BTBP in bulk polystyrene (7 μm film). The solid line indicates a fit of the bulk data to the Vogel−Tammann−Fulcher (VTF) equation. As expected, the temperature dependence of the bulk polystyrene data above $T_{g,DSC}$ is similar to that measured by dielectric relaxation,[22-24] and below $T_{g,DSC}$ a sharp break in the temperature dependence is seen.

The key feature in Figure 3 is that the slow decay process in the thin-film data matches the single-step decay observed in bulk samples. This is true both for the reorientation times shown in Figure 3 and for the KWW β parameter values (average β = 0.77 for the bulk and 0.76 for the slow process in thin films). *Thus, we attribute the slow decay process to a subset of probe molecules with bulk-like dynamics and the fast decay process to a subset of probes with much faster dynamics.* In the higher temperature range (>$T_{g,DSC}$), where the time scale of the slow process becomes comparable to that of the fast process, the isothermal anisotropy data on thin films were fitted to a single KWW function (green squares). In these fits, the rotation times are similar to the bulk

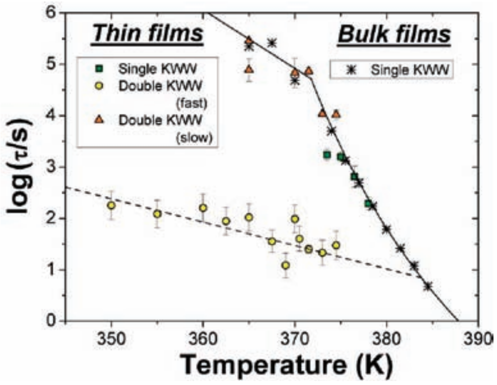

Figure 3. Reorientation times for BTBP in freestanding films of PS(160k) at different temperatures. Below 375 K, a fast subset of probe molecules is observed; the dashed line indicates the temperature dependence of this process. The solid curved line is a VTF fit to data from bulk samples above $T_{g,DSC}$; the fit parameters are $\log(\tau_0/s) = -10.3$, $B = 1255$ K, and $T_0 = 335$ K. The solid line describes the bulk data below $T_{g,DSC}$.

values, but the β values are lower (~0.51). This is consistent with the existence of a fast process in thin films (18−28 nm) whose relaxation time is too close to that of the bulk process to be resolved by fitting. Whether this convergence of the fast and bulk processes is complete at higher temperatures ($>T_{g,DSC} + 5$ K) is an important question that cannot be answered for freestanding films due to their instability at such temperatures. However, such a conclusion would be consistent with studies of supported polystyrene films by broadband dielectric spectroscopy and nanocalorimetry;[25,26] these papers report no evidence of a fast process in the accessible temperature range ($>T_g + 7$ K).

These photobleaching experiments provide some information about the fast subset of probes. Figure 3 shows that the fast subset reorients in a few hundred seconds throughout the temperature range 350−375 K. Because of the limited time resolution of the present apparatus, there is considerable scatter in the reported times, and we cannot reliably determine the KWW β parameter for the fast subset. We attempted experiments below 350 K, but the amplitude of the fast process became so small that reliable data could not be obtained. The fast process is weakly temperature dependent, with an activation energy of roughly 100 kJ/mol. This is similar to the temperature dependence of surface relaxation probed by atomic force microscopy.[28]

In the narrow temperature range where both the fast and slow processes can be measured (near $T_{g,DSC} - 5$ K), their relaxation times differ by 4 orders of magnitude. Since both the fast and slow processes were observed in films as thin as 18 nm, we conclude that a significant fraction of an 18 nm film has bulk-like molecular mobility at $T_{g,DSC} - 5$ K. While Figure 2 shows that this bulk-like fraction decreases with increasing temperature, our uncertainty in estimating the anisotropy value at $t = 0$ limits our ability to quantify this fraction from the isothermal experiments.

Temperature-ramping anisotropy experiments are well-suited for quantifying the fraction of the probes in the fast subset. The bulk-like fraction cannot be responsible for the early decay of the anisotropy curves shown in Figure 1, since no decay is observed for the bulk sample (3 μm) below 365 K. In this temperature range, the amount of the decay can be interpreted as the fraction of the film with fast dynamics. The fractions calculated in this manner are consistent with those estimated from isothermal measurements, such as those shown in Figure 2. It is also possible

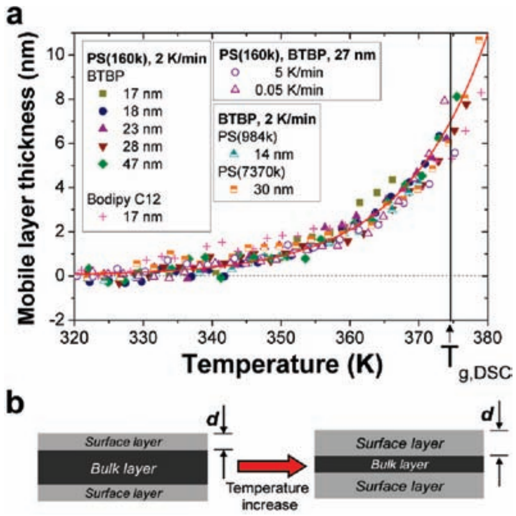

Figure 4. (a) Mobile surface layer thickness for polystyrene which depends upon temperature but does not depend upon total film thickness, polymer molecular weight, probe molecule identity, or temperature scanning rate. (b) Schematic model showing a mobile surface layer whose thickness grows with temperature.

to fit our data with a single continuous distribution of relaxation times instead of the two-state model that we have adopted. While this view is physically appealing, we utilize the two-state model as the simplest description consistent with the data. This approach has the advantage of focusing attention on the fraction of the probes that have dynamics that deviate strongly from bulk behavior.

In light of recent studies showing that free surfaces can strongly influence T_g,[13,14] it is reasonable to assume that the fast subset of probe molecules is located near the surfaces of the freestanding polymer films.[27−29] Using this and the assumption that the probes are uniformly dispersed in the thin films, we can calculate the thickness of the mobile surface layer $d(T)$ as

$$d(T) = \frac{D}{2}\left[1 - \left\{\frac{r(T)}{r(i)}\right\}_{tf} \Big/ \left\{\frac{r(T)}{r(i)}\right\}_{bf}\right] \qquad (1)$$

Here D is the measured film thickness and the subscripts “tf” and “bf” stand for thin film and bulk film, respectively. Equation 1 can only be utilized in the temperature range where the bulk reorientation is reasonably slow ($<T_{g,DSC}$).

Figure 4a shows that the thickness of the mobile surface layer calculated from eq 1 increases with temperature for freestanding polystyrene films and is about 7 nm at $T_{g,DSC}$. As shown in the figure, the mobile surface layer thickness determined in this manner is independent of ramping rate, molecular weight, and total film thickness. The latter two observations strongly support the assumption that the fast subset of probe molecules is located near the free surface of the films. We know of no other viewpoint that can collapse all the data shown in Figure 1 (and additional data shown in the SI, Figure 4S) onto the single curve shown in Figure 4a. Figure 4a also includes data from temperature-ramping anisotropy measurements using a different probe. Even though Bodipy C12 reorients 30 times faster than BTBP (see SI, Figure 1S), the mobile layer thickness deduced from these experiments agrees with the rest of the data. In addition, measurements on a probe covalently attached to one end of polystyrene chains also agree with the result shown in Figure 4a (measurements shown in Figure 4S in the SI). This consistency of results for the two dispersed probes and the tethered probe supports the view that the probes are uniformly distributed in the films and that they are reliable reporters of polymer dynamics.

Figure 4b shows a schematic model of a freestanding polymer film constructed on the basis of these findings. While the interior of the film follows the bulk dynamics, regions near the free surfaces (with thickness $d(T)$) show significantly faster dynamics. The mobile surface layer initiates around 330 K and grows exponentially with temperature. Since the dynamics near the surface have a weaker temperature dependence, the difference in the dynamics between the surface and the interior gets smaller as the temperature approaches $T_{\mathrm{g,DSC}}$ from below.

Our observation that the thickness of the mobile surface layer grows with increasing temperature is qualitatively similar to observations by Herminghaus et al.[30,31] They studied polystyrene emulsions by NMR and deduced that $d(T)$ grows continuously according to $d(T) \propto (T_{\mathrm{g}} - T)^{-1}$. The depth to which nanoparticles embed on a polystyrene surface has also been well-described by an exponential growth function.[32] In that study, the depth reaches 5.5 nm at $T_{\mathrm{g}} - 10$ K, as compared to the 3 nm mobile surface layer estimated at this temperature in the current work. From Figure 4a, the surface mobile layer thickness at $T_{\mathrm{g,DSC}}$ is estimated as 7 nm. This value is similar to the 3.8 nm mobile layer thickness deduced from a calorimetric study of suspended polystyrene spheres.[33] From our results, we conclude that freestanding polystyrene films thicker than 14 nm have a bulk-like portion of the film in the interior even at $T_{\mathrm{g,DSC}}$. This may account for the resistance that such films show toward hole formation and growth. In spite of a large T_{g} reduction, hole formation and growth is nearly independent of film thickness for films as thin as 50 nm.[7−9] A bulk-like interior region also explains why a dynamic secondary ion mass spectrometry study reported no enhancement of probe diffusion normal to the surface of freestanding film as thin as 33 nm.[34]

In summary, molecular mobility in freestanding polystyrene films was studied in films as thin as 14 nm. Isothermal anisotropy measurements provide clear evidence of two subsets of probe molecules with distinct dynamics. Temperature-ramping measurements allow the fraction of each subset to be quantified as a function of temperature. The slow subset of probes exhibits bulk-like dynamics, and we attribute the fast subset to probes near the free surfaces. Probes near the free surface reorient within a few hundred seconds, even at $T_{\mathrm{g,DSC}} - 25$ K, while probes in the interior of the film reorient roughly 4 orders of magnitude slower. The thickness of the mobile surface layer increases with increasing temperature and does not depend on the total film thickness, the molecular weight of the polymer, or other control parameters for the experiment. The estimated thickness of the mobile surface layer thickness for polystyrene is 7 nm at $T_{\mathrm{g,DSC}}$. We do not anticipate that this value is universal for polymers, and further measurements will be required to understand its origin.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Alcoutlabi, M.; McKenna, G. B. *J. Phys.: Condens. Matter* **2005**, *17*, R461–R524.

(2) Dalnoki-Veress, K.; Forrest, J. A.; Murray, C.; Gigault, C.; Dutcher, J. R. *Phys. Rev. E* **2001**, *63*, 031801.

(3) Forrest, J. A.; Dalnoki-Veress, K. *Adv. Colloid Interface Sci.* **2001**, *94*, 167–196.

(4) Forrest, J. A.; Dalnoki-Veress, K.; Dutcher, J. R. *Phys. Rev. E* **1997**, *56*, 5705–5716.

(5) Kim, S.; Roth, C. B.; Torkelson, J. M. *J. Polym. Sci., Part B: Polym. Phys.* **2008**, *46*, 2754–2764.

(6) Liem, H.; Cabanillas-Gonzalez, J.; Etchegoin, P.; Bradley, D. D. C. *J. Phys.: Condens. Matter* **2004**, *16*, 721–728.

(7) Roth, C. B.; Dutcher, J. R. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 3011–3021.

(8) Roth, C. B.; Dutcher, J. R. *Phys. Rev. E* **2005**, *72*, 021803.

(9) Xavier, J. H.; Pu, Y.; Li, C.; Rafailovich, M. H.; Sokolov, J. *Macromolecules* **2004**, *37*, 1470–1475.

(10) O'Connell, P. A.; McKenna, G. B. *Eur. Phys. J. E* **2006**, *20*, 143–150.

(11) Rotella, C.; Napolitano, S.; Wuebbenhorst, M. *Macromolecules* **2009**, *42*, 1415–1417.

(12) Napolitano, S.; Wubbenhorst, M. *Polymer* **2010**, *51*, 5309–5312.

(13) Sharp, J. S.; Forrest, J. A. *Phys. Rev. Lett.* **2003**, *91*, 235701.

(14) Ellison, C. J.; Torkelson, J. M. *Nat. Mater.* **2003**, *2*, 695–700.

(15) Ediger, M. D. *Annu. Rev. Phys. Chem.* **1991**, *42*, 225–250.

(16) Inoue, T.; Cicerone, M. T.; Ediger, M. D. *Macromolecules* **1995**, *28*, 3425–3433.

(17) Lee, H. N.; Paeng, K.; Swallen, S. F.; Ediger, M. D. *Science* **2009**, *323*, 231–234.

(18) Paeng, K.; Lee, H. N.; Swallen, S. F.; Ediger, M. D. *J. Chem. Phys.* **2011**, *134*, 024901.

(19) Lee, H. N.; Paeng, K.; Swallen, S. F.; Ediger, M. D. *J. Chem. Phys.* **2008**, *128*, 134902.

(20) Thurau, C. T.; Ediger, M. D. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 2463–2472.

(21) Wang, C. Y.; Ediger, M. D. *Macromolecules* **1997**, *30*, 4770–4771.

(22) Svanberg, C. *Macromolecules* **2007**, *40*, 312–315.

(23) van den Berg, O.; Sengers, W. G. F.; Jager, W. F.; Picken, S. J.; Wubbenhorst, M. *Macromolecules* **2004**, *37*, 2460–2470.

(24) Roland, C. M.; Casalini, R. *J. Chem. Phys.* **2003**, *119*, 1838–1842.

(25) Mapesa, E. U.; Erber, M.; Tress, M.; Eichhorn, K. J.; Serghei, A.; Voit, B.; Kremer, F. *Eur. Phys. J.—Special Topics* **2010**, *189*, 173–180.

(26) Tress, M.; Erber, M.; Mapesa, E. U.; Huth, H.; Muller, J.; Serghei, A.; Schick, C.; Eichhorn, K. J.; Volt, B.; Kremer, F. *Macromolecules* **2010**, *43*, 9937–9944.

(27) Wallace, W. E.; Fischer, D. A.; Efimenko, K.; Wu, W. L.; Genzer, J. *Macromolecules* **2001**, *34*, 5081–5082.

(28) Fakhraai, Z.; Forrest, J. A. *Science* **2008**, *319*, 600–604.

(29) Agra, D. M. G.; Schwab, A. D.; Kim, J. H.; Kumar, S.; Dhinojwala, A. *Europhys. Lett.* **2000**, *51*, 655–660.

(30) Herminghaus, S.; Seemann, R.; Landfester, K. *Phys. Rev. Lett.* **2004**, *93*, 017801.

(31) Herminghaus, S. *Eur. Phys. J. E* **2002**, *8*, 237–243.

(32) Ilton, M.; Qi, D.; Forrest, J. A. *Macromolecules* **2009**, *42*, 6851–6854.

(33) Sasaki, T.; Shimizu, A.; Mourey, T. H.; Thurau, C. T.; Ediger, M. D. *J. Chem. Phys.* **2003**, *119*, 8730–8735.

(34) Pu, Y.; White, H.; Rafailovich, M. H.; Sokolov, J.; Patel, A.; White, C.; Wu, W. L.; Zaitsev, V.; Schwarz, S. A. *Macromolecules* **2001**, *34*, 8518–8522.