Small Molecule Probe Diffusion in Thin and Ultrathin Supported Polymer Films

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ABSTRACT: The translational diffusion of two small molecule probes, decacyclene and lophine, has been studied in supported polymer films as a function of film thickness using fluorescence nonradiative energy transfer. These probes are sufficiently large that their translational motion is coupled substantially to the segmental mobility of the polymer matrix. Probe diffusion in polystyrene films on fused quartz substrates was found to slow as film thickness is decreased below approximately 150 nm. In contrast, no change in probe diffusion as compared to bulk values was found in poly(isobutyl methacrylate) films as thin as 50 nm and poly(2-vinylpyridine) films as thin as 88 nm. These differences cannot be explained in terms of differences in polymer affinity for the fused quartz substrate, indicating that polymer−substrate affinity does not influence probe diffusion in this film thickness range. Probe diffusion toward polymer−substrate and polymer−free surface interfaces has also been studied with little change in diffusive behavior as compared to bulk in regions as close as 40 nm from the interface. This indicates that the range of influence of a particular polymer−free surface or polymer−substrate interaction is of limited extent (<40 nm distance) in modifying thin and ultrathin behavior.

Introduction

Recently, a significant body of experimental evidence has indicated that polymer properties in "ultrathin" films (thickness < ∼200 nm) may be substantially different than those found in the "bulk" state. Changes in glass transition temperature (T_g),[1−10] phase behavior,[11−16] crystallization,[17−20] chain conformation,[21,22] permeability,[23,24] polymer self-diffusion,[25] dewetting,[26,27] and relaxation dynamics[28] with film thickness have been observed or inferred. Deviations from bulk behavior have been reported for film thicknesses as large as 500 nm but are more frequently reported for film thicknesses of 100 nm or less. Whether the film is freely standing or supported and the level of polymer−substrate affinity are apparently of key importance in defining the extent of deviation from bulk properties.

Changes in film behavior with thickness may be traced to the enhanced role of interfacial regions as thickness is decreased. Polymer chains near an interface may have substantially different properties than those in the bulk.[29−35] This may be due to specific interactions between the polymer and interface such as adsorption or may be due to chain conformational changes attributable to the presence of a boundary. Generally, an impenetrable interface such as a solid substrate is thought to reduce the mobility of polymer chains near it through a reduction in conformational entropy. Strong positive interactions between the polymer and substrate may also "tie" portions of the chain to the interface. Studies of polymer diffusion near a solid substrate have indicated a reduction in polymer mobility closer to the substrate[36,37] that has been interpreted as being associated with an increase in effective T_g. (Such an interpretation is consistent with observations of higher T_g's in filled polymers than in unmodified homopolymers.[29]) In contrast, the air−polymer interface or "free" surface is often thought of as a region of enhanced mobility. Simulations indicate that this free surface region may have decreased density as compared to the bulk.[31] It has also been argued that chain-end segregation to a surface due to conformational entropy considerations may increase local free volume and thus increase polymer mobility.[32] Brillouin scattering studies of freely standing, ultrathin polystyrene films have indicated substantial reductions in T_g as thickness is reduced.[9,10] Positron annihilation lifetime spectroscopy,[38,39] atomic force microscopy,[40−44] buffing,[45] and bonding[46,47] experiments probing the free surface region of polymer films have also indicated enhanced mobility; however, recent near-edge X-ray absorption fine structure spectroscopy measurements[48] found no evidence for enhanced polymer mobility at the free surface.

In supported polymer films, where there are both a free surface and a substrate interface, an interplay between the two competing interfacial effects may be expected, with overall film properties being determined by whichever effect dominates. Ellipsometry[2−4] and X-ray reflectivity[5−8] studies of supported films have suggested that polymer−substrate affinity is the deciding factor in determining which effect dominates. Systems with strong interactions between the polymer and substrate showed increases in T_g with decreasing film thickness while those with weak interactions showed decreases in T_g. Specific interactions between the polymer and substrate have also been found to be of importance in thin-film crystallization[19] and in interfacial chain conformations.[22] However, studies of filled polymer systems have shown that specific chemical interactions between the filler and polymer play a minor role in chain mobility.[29] Of primary importance in

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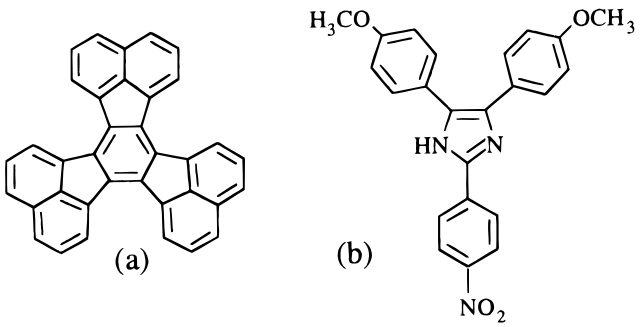

Figure 1. Small molecule probes: (a) decacyclene and (b) lophine.

understanding this behavior is to determine how far effects due to specific polymer−substrate interactions propagate away from the interface. Typically, these types of interactions are thought to be very local in nature and only to affect chains in the immediate vicinity of the surface. Therefore, they would not be expected to propagate much farther than one or two radii of gyration (R_g) away from the substrate and should only be important in films with thicknesses comparable to this value.

Recent work involving polymer chain diffusion near solid substrates and also in ultrathin films has suggested that the range of influence of the substrate may be much greater than anticipated. Zheng et al.,[36] using dynamic scanning ion mass spectrometry, interpreted data to find that diffusion rates perpendicular to the substrate were as much as an order of magnitude slower than in bulk even up to 80 nm ($10R_g$) away from the substrate. Smaller, yet nevertheless substantial, decreases in lateral polymer diffusion coefficients were found in films as thick as 150 nm ($50R_g$) by Frank et al.[25] Both of these studies involved polystyrene (PS) and silicon oxide substrates that have a relatively weak affinity for one another. These results have been explained in terms of increases in polymer T_g; however, *decreases* in T_g have been found for this same system in ellipsometry,[10] X-ray reflectivity,[5] and dewetting experiments.[26,27] Also, work by Lin et al.[37] on poly(methyl methacrylate) (PMMA) diffusion away from a silicon oxide surface found that the range of influence of the substrate on polymer diffusion was at most 40 nm ($4R_g$). PMMA would be expected to have a significantly stronger affinity for the silicon oxide substrate than PS. The reasons for these differences are not clear and warrant further research.

Here we address these issues by considering how diffusion of small molecule probes with motions substantially coupled to the cooperative segmental mobility or polymer α-relaxation dynamics may be affected by thickness in ultrathin, supported films and by differing polymer−substrate interactions. Such studies are also important technologically for applications of thin and ultrathin polymer films as barrier coatings and in membranes. Specifically, fluorescence nonradiative energy transfer (NRET) is used to study the translational diffusion of two small molecule probes, decacyclene and lophine (see Figure 1), in polymer films as thin as 50 nm. Decacyclene and lophine are sufficiently large in size such that their motion is coupled substantially to the cooperative segmental mobility of the polymer α-relaxation and therefore are sensitive to changes in T_g and polymer cooperative segmental mobility that may occur as film thickness is reduced. The role of polymer−substrate affinity will specifically be studied by measuring probe diffusion in three polymer matrices: PS, poly(isobutyl methacrylate) (PiBMA), and poly(2-vinylpyridine) (P2VP), each expected to have different affinity for the fused quartz substrates employed. Also, probe diffusion near the free surface and polymer−substrate interface will be explored to allow estimation of the range of influence of each of these interfaces on diffusion.

Experimental Section

Measuring Small Molecule Diffusion via NRET. Fluorescence NRET occurs when an excited "donor" species transfers its energy to an "acceptor" species via Coulombic dipole−dipole interactions. The rate parameter for energy transfer, k_T, from donor to acceptor is given by[49]

$$k_T = \frac{1}{\tau_d}\left(\frac{R_0}{r}\right)^6 \tag{1}$$

where τ_d is the excited-state lifetime of the donor in the absence of acceptor, r is the distance between the donor and acceptor, and R_0 is the Förster radius which is the distance at which the efficiency of energy transfer is 50%. Since R_0 is typically between 2 and 5 nm for most donor−acceptor pairs,[50] k_T is very sensitive to distances of comparable length, making NRET attractive for measuring diffusion over small distances such as those found in ultrathin polymer films.

Small molecule diffusion is measured with NRET by employing a bilayer of two thin polymer films. One film contains polymer that has a small amount of donor species (in this case pyrene) covalently attached to the chains. The other film contains acceptor molecules (decacyclene or lophine) freely doped in the polymer.[51] The films are layered on top of one another and then annealed. (Unless otherwise specified, the donor-labeled film is layered on top of the acceptor-doped film that is sitting on the substrate.) The acceptor molecules will then diffuse into the donor film, resulting in a net decrease in donor fluorescence intensity due to NRET. Over the time scale of the experiment, the donor chromophores are essentially immobile in comparison to the acceptor molecules since they are attached to the polymer. If one assumes Fickian diffusion of the acceptor molecules, the decrease in steady-state donor fluorescence intensity or energy-transfer efficiency, $E(t)$, can be related to the translational diffusion coefficient of the acceptor molecule, D:[52]

$$E(t) = \frac{I(0) - I(t)}{I(0)} = K\left(\frac{\sqrt{Dt}}{w}\right) \quad \text{for } t \le w^2/(16D) \tag{2}$$

where $I(0)$ is the initial steady-state donor fluorescence intensity, $I(t)$ is the steady-state donor fluorescence intensity at annealing time, t, w is the donor-layer thickness, and K is a constant that depends on the initial acceptor concentration and R_0.[53] For a more thorough discussion on the use of NRET to measure diffusion in thin polymer films, see refs 52 and 54.

Materials and Sample Preparation. Pyrene-labeled monomer was synthesized by reacting 1-pyrenemethanol with methacryloyl chloride in the presence of triethylamine in tetrahydrofuran at 0 °C.[55] Pyrene-labeled polymers were synthesized by copolymerizing pyrene-labeled monomer with styrene, isobutyl methacrylate, or 2-vinylpyridine monomer in dimethylformamide (DMF) at 70 °C using AIBN initiator. Molecular weights and pyrene-label content as determined by UV/vis spectroscopy were as follows. PS: $M_w = 121\,000$, $M_w/M_n = 1.7$ (GPC), label content = 0.005 (moles pyrene label/moles polymer repeat unit); PiBMA: $M_w = 310\,000$, $M_w/M_n = 1.8$ (GPC with reference to PMMA standards), label content = 0.009; P2VP: $M_w \approx 600\,000$ (intrinsic viscosity measurements[56] in DMF at 50 °C), label content = 0.006. Unlabeled

homopolymers were polymerized under identical conditions. PS: $M_w = 125\,000$, $M_w/M_n = 1.7$; PiBMA: $M_w = 320\,000$, $M_w/M_n = 1.9$; P2VP: $M_w \approx 600\,000$. Pyrene-labeled polymer was mixed with unlabeled homopolymer to give an overall pyrene-label content of between 0.0012 and 0.003 mole fraction (reference to repeat unit concentration) in the donor films. Acceptor films contained unlabeled homopolymer doped with 0.0002−0.0008 mole fraction decacyclene or 0.0021−0.0056 mole fraction lophine. R_0 is 3.7 nm for the pyrene/decacyclene donor−acceptor pair and 3.2 nm for the pyrene/lophine donor−acceptor pair. The bulk polymer T_g's measured by DSC (onset, 10 °C/min) were approximately (±0.5 °C) 100 °C for PS, 64 °C for PiBMA, and 98 °C for P2VP. Addition of the decacyclene and lophine probes did not change T_g measurably.

Films were spun[57] from dilute solutions of toluene, 2-butanone, or chloroform depending on the polymer−probe system. Films were placed under vacuum for at least 24 h at room temperature to remove residual solvent, and thicknesses were measured using a Tencor P10 profilometer. PS and PiBMA donor or acceptor films were floated off glass slides onto the surface of a deionized water bath and then layered on top of the complementary film that was spun onto an acid-cleaned fused quartz plate. P2VP films adhered very strongly to the glass slides and therefore could not be floated off. Instead, P2VP films were spun onto polished NaCl IR windows, and the interface was dissolved away with deionized water. Layered films were then placed under vacuum at room temperature for another 24 h to remove any residual water.[58] This drying procedure was deemed sufficient since drying for longer time periods and at slightly increased temperatures produced no significant change in the measured diffusion coefficients.[58]

Fluorescence Measurements. Steady-state fluorescence intensity measurements were performed in situ, using a Spex Fluorolog spectrophotometer equipped with a temperature-controlled sample cell. Samples were excited at the pyrene absorbance maximum (between 328 and 346 nm depending on the polymer), and the fluorescence emission was monitored as a function of time at either 375 or 397 nm. Thermal equilibrium was attained approximately 30−60 s after the sample was loaded into the cell, and this was when the first intensity measurement was taken ($t = 0$). All intensity measurements were corrected for background noise.[59] Some photobleaching of the pyrene-labeled PS and P2VP could be observed at high temperatures. This effect was minimized by flowing dry nitrogen through the sample chamber and employing conditions and time scales where it was not an important factor.

Results and Discussion

To measure appropriately small molecule diffusion in ultrathin films with NRET, several considerations must be taken.[59] Probe diffusion must be slow enough to characterize accurately with NRET. There must not be significant diffusion during the approach to thermal equilibrium, and it is also beneficial for measurements to be taken only in the linear regime of the Fickian diffusion equation solution, i.e., when $t \leq w^2/16D$. This means that D must be less than approximately 4×10^{-15} cm^2/s to measure diffusion over an appropriate time scale (with the systems used here, about 300 s) for $w = 45$ nm. One way to achieve this is by using large probes and annealing at temperatures close to T_g.[52,60,61] This is fortunate because these are also the conditions that will give us the most information about the α-relaxation in these films. Any shift in T_g due to film thickness will have its greatest effect on polymer properties at temperatures near T_g since this is the temperature range in which α-relaxation dynamics are most temperature dependent. Other potential concerns regarding the use of NRET to study diffusion in ultrathin films[51,53] involve energy transfer across interfaces and also appropriate probe diffusion distances such that a Fickian concentration profile may develop, issues considered unimportant for films thicker than 20 nm (single-layer film thickness).

It has been demonstrated[52,60,62] that the temperature dependence of the diffusion of appropriately sized small molecule probes in rubbery polymers near T_g may be described by a modified Williams−Landel−Ferry[63] (WLF) equation:

$$\log\left[\frac{D(T)}{D(T_g)}\right] = \frac{\xi C_1 (T - T_g)}{C_2 + T - T_g} \tag{3}$$

where C_1 and C_2 are the WLF parameters of the polymer matrix. In the context of the Vrentas−Duda free volume theory,[64,65] ξ may be interpreted to be the ratio of the solute (probe) jumping unit volume to that of the polymer matrix jumping unit. The parameter ξ has also been interpreted as reflecting the degree to which the solute translational diffusion is coupled to the polymer matrix α-relaxation processes,[62] with $\xi = 1$ being complete coupling.

Recently, it has been demonstrated that, in rubbery polymers near T_g, sufficiently large probes exhibit average rotational reorientation dynamics identical to the polymer cooperative segmental dynamics at the same time that the probe translational diffusivities have temperature dependencies significantly less than those of average reorientation or α-relaxation processes.[52,60,61,66,67] This effect is sometimes referred to as the translation−rotation paradox for diffusion.[66,68,69] A recent experimental study[66] has demonstrated that the paradox holds in the polymeric rubbery state near T_g but that in the quenched glassy state similar temperature dependencies are recovered for probe rotational and translational diffusion. This study further demonstrated a strong temperature dependence of the breadth of the relaxation distribution in the rubbery state near T_g but a temperature invariance of the breadth of the relaxation distribution in the quenched glassy state. The paradox can be explained[66] by understanding that average probe rotational diffusion and average probe translational diffusion reflect different portions of the relaxation distribution (rotation the long-time side, translation the short-time side). This yields different temperature dependencies for average rotational diffusion and average translational diffusion for temperature ranges where relaxation dynamics are thermorheologically complex and similar temperature dependencies where relaxation dynamics are thermorheologically simple. Related explanations have been offered by other researchers,[67−70] and related phenomena have been observed in low-molecular-weight glass formers as well.[71]

Given this understanding, ξ simply reflects the fact that differently sized and shaped probes[52,61] will not be able to couple to the same breadth of the polymer relaxation distribution, differing in the extent to which they may be able to relax in association with the fastest-relaxing, smallest cooperatively rearranging regions. Thus, a value of ξ near 1 indicates that the probe is so large that many of the small, fast-relaxing cooperatively rearranging regions in the polymer have essentially no effect on the probe dynamics.

The temperature dependence of D for decacyclene and lophine in "bulk" PiBMA films is given in Figure 2 along

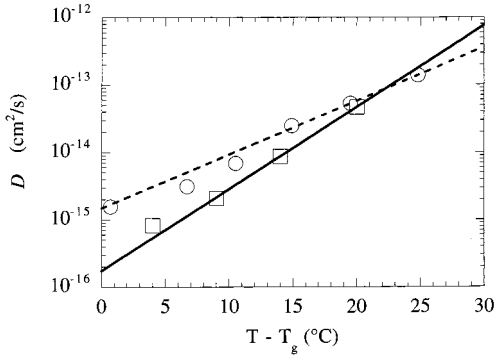

Figure 2. Temperature dependence of D for (□) decacyclene and (○) lophine in "bulk" PiBMA films. Curves are fits to eq 3 with $\xi = 0.73$ and $D(T_g) = 1.7 \times 10^{-16}$ cm^2/s for decacyclene (solid curve) and $\xi = 0.48$ and $D(T_g) = 1.5 \times 10^{-15}$ cm^2/s for lophine (dashed curve). In eq 3, $C_1 = 13$ and $C_2 = 58$ K.[52]

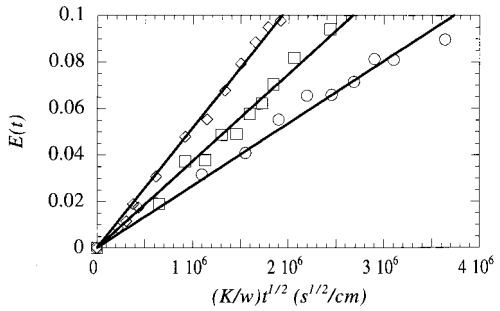

Figure 3. $E(t)$ vs $(K/w)t^{1/2}$ for decacyclene diffusion in PS films of thickness (◇) 367, (□) 124, and (○) 66 nm at 103 °C. Straight lines are linear fits with slope equal to $D^{1/2}$. (Thickness is for the total bilayer film with donor and acceptor layers of equal thickness.)

with fits to eq 3. For decacyclene, with an estimated probe volume[72] of 314 cm^3/mol, $\xi = 0.73$. Lophine is smaller in size and differently shaped, with an estimated probe volume[72] of 277 cm^3/mol and $\xi = 0.48$. For both probes, D is small enough in the immediate vicinity of T_g so that probe diffusion in ultrathin films may be measured in films as thin as 50 nm.

Probe diffusion was measured in thin and ultrathin films of PS, PiBMA, and P2VP on fused quartz substrates. Fused quartz has a polar surface, due to the presence of hydroxyl groups at the surface. PS is a nonpolar polymer and therefore should not have strong interactions with the fused quartz substrate. In fact, PS has been observed to dewet similar silicon oxide surfaces.[27,73] The carbonyl group in the side chain of PiBMA may undergo hydrogen bonding with the fused quartz surface and thus would be expected to have a more favorable interaction with the substrate than PS. However, it is still possible to float PiBMA films off quartz slides. P2VP is very polar and should have strong favorable interactions with the fused quartz. P2VP adheres strongly to fused quartz substrates, and it was impossible to float P2VP films off quartz slides.

Figure 3 plots $E(t)$ vs $(K/w)t^{1/2}$ for decacyclene diffusion in PS for films 367, 124, and 66 nm thick (this is the overall bilayer film thickness, with approximately equal donor and acceptor layer thicknesses) at $T = 103$ °C. Since the slope of each data set equals $D^{1/2}$, there is a decrease in probe diffusivity with decreasing thickness in ultrathin PS films. (Note that the very good linearity of the data even from short annealing times argues against any significant modification of our measured diffusion coefficients associated with unusual or unanticipated probe segregation or probe orientation phenomena.[51])

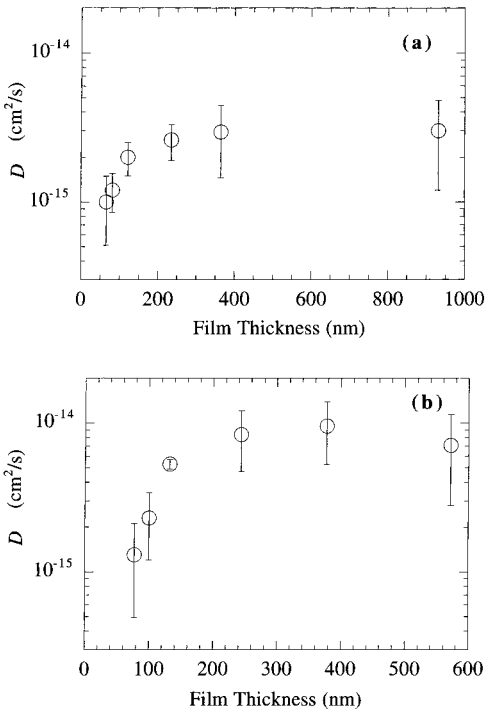

Figure 4. D as a function of film thickness for (a) decacyclene and (b) lophine diffusion in PS at 103 °C. (Thickness is for the total bilayer film with donor and acceptor layers of equal thickness.)

Figure 4 plots D as a function of PS film thickness for decacyclene and lophine. Each data point represents the mean value of D for 3−8 different films of approximately the same film thickness with error bars reflecting the standard deviation about the mean. For both probes, there is a slowing of diffusion when film thickness is decreased below approximately 150 nm. This is qualitatively similar to the results of Frank et al.[25] that show a slowing of lateral diffusion of PS chains in films thinner than 150 nm; it has been proposed[74] that the results of Frank et al.[25] may be due to an increase in T_g of 7 °C for PS films less than 100 nm thick. In the thinnest film we examined, 67 nm, D is reduced to approximately one-third of its bulk value for decacyclene in PS. By interpreting the small molecule diffusion results presented here in a manner similar to the results for polymer diffusion by Frank et al.,[25,74] one may calculate an "apparent" shift in T_g of +2.5 °C as compared to bulk for the 67 nm thick film. (Such a calculation is done by assuming that eq 3 holds and using the parameters for decacyclene diffusion in PS:[52] $\xi = 0.63$, $C_1 = 15$, and $C_2 = 40$ K.) However, as noted previously, this interpretation is apparently not in agreement with other studies of ultrathin PS films on silicon oxide[5,10,26,27] which found a decrease in T_g with decreasing film thickness. Before conclusions are reached regarding the reduction in probe diffusivity with decreasing film thickness being associated with an increase in the system T_g, it is important to determine whether such modifications of diffusivity are general for a range of polymer−probe systems.

Example plots of $E(t)$ vs $(K/w)t^{1/2}$ for decacyclene and lophine diffusion in PiBMA films are given in Figure 5, and decacyclene and lophine diffusivities in PiBMA films as a function of thickness at $T = 72$ °C are given

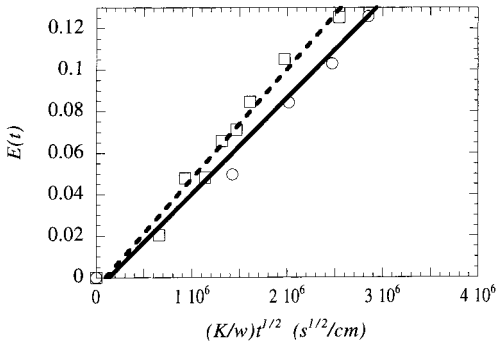

Figure 5. $E(t)$ vs $(K/w)t^{1/2}$ for decacyclene (□) and lophine (○) diffusion in PiBMA at 72 °C. Film thicknesses are 69 nm for the decacyclene system and 60 nm for the lophine system. Straight lines are linear fits with slope equal to $D^{1/2}$. (Thickness is for the total bilayer film with donor and acceptor layers of equal thickness.)

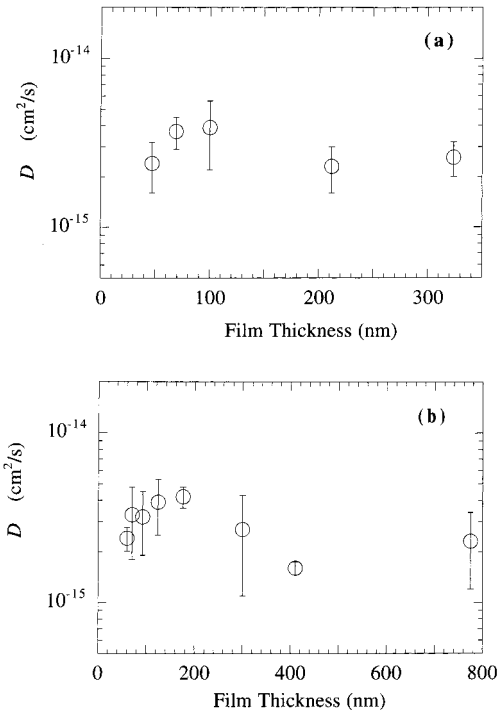

Figure 6. D as a function of film thickness for (a) decacyclene and (b) lophine diffusion in PiBMA at 72 °C. (Thickness is for the total bilayer film with donor and acceptor layers of equal thickness.)

in Figure 6. Similar to the results in Figure 3 for PS, the linearity of the data in Figure 5 indicates that in PiBMA there is no significant modification of our measured diffusion coefficients associated with unusual or unanticipated probe segregation or probe orientation phenomena.[51] However, in contrast to the PS results, Figure 6 clearly indicates that for PiBMA films there is no change in D with film thickness, within experimental error, even for films as thin as 50 nm. Consistent with this result, ellipsometry studies of PMMA films on SiO_2, which should have polymer−substrate interactions similar to PiBMA on quartz, showed no discernible change in T_g for films of comparable thickness.[3] It is also consistent with a nonlinear optical study of the relaxation dynamics of ultrathin isobutyl methacrylate copolymer films on quartz that showed no evidence of significant T_g changes in films as thin as 7 nm.[28] However, the nonlinear optical study also showed a broadening of the distribution of α-relaxation times in

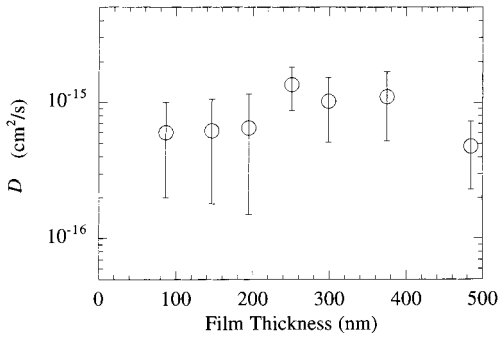

Figure 7. D as a function of film thickness for decacyclene diffusion in P2VP at 101 °C. (Thickness is for the total bilayer film with donor and acceptor layers of equal thickness.)

films thinner than 150 nm, with the increase in breadth occurring predominantly at the shortest relaxation times. Translational diffusion of small molecule probes may be expected to be sensitive to changes in the short-time portion of the polymer relaxation distribution,[66] and thus translational diffusion may appear enhanced with a broadening of the distribution. Figure 6 shows no such increase in D with decreasing film thickness.

The reason for this may be explained in terms of the origin of the relaxation distribution broadening in ultrathin polymer films and how we measure probe translational diffusion. It has been proposed that the broadening of the relaxation distribution in ultrathin polymer films is due to the increased influence of free surface and/or substrate interfacial regions on the overall relaxation dynamics of the film. In our probe translational diffusion studies, we have restricted ourselves to the linear regime of Fickian diffusion equation solution, $t \leq w^2/16D$, which essentially means that the diffusing species has not translated far enough for its concentration profile to be in contact with the opposite bounding interface. If the interfacial regions in which the polymer relaxation dynamics are modified as compared to bulk do not extend far into the film, few probe molecules may diffuse into their range of influence over the time scales we are observing. In other words, the results of the present study and our recent nonlinear optical characterization of polymer α-relaxation processes in ultrathin PiBMA films[28] are consistent. However, it must be appreciated that the diffusion measurements are insensitive to regions extremely close to the polymer−substrate and polymer−air interfaces of the ultrathin films while the nonlinear optical study measures behavior from the entirety of the ultrathin polymer films, including within several nanometers of the polymer−substrate and polymer−air interfaces. (Apparently, the regions within a few nanometers of the interfaces account for much of the observed broadening of the α-relaxation distribution in ultrathin polymer films.)

Figure 7 shows decacyclene diffusion in P2VP films at $T = 101$ °C. Similar to the results for PiBMA, and in contrast to the results for PS, there is no substantial effect of film thickness on probe diffusion. (Also similar to the results for PS and PiBMA films, there was very good linearity in the plots of $E(t)$ vs $(K/w)t^{1/2}$ for decacyclene in P2VP, indicating that unanticipated probe segregation or orientation phenomena were not significantly affecting the measured probe diffusion coefficients.[51]) Lophine diffusion in P2VP was also measured. However, the data are not reported in a figure due to the low values of D measured, in some

cases an order of magnitude lower than those observed for decacyclene at similar film thickness. These low diffusivities are necessarily accompanied by very significant experimental uncertainties, making the reporting of the data in a figure tenuous at best. These abnormally low diffusion coefficients are likely associated with the ability of lophine to undergo hydrogen bonding with the P2VP matrix, thereby slowing the local dynamics in comparison to probe−polymer systems, such as decacylene−P2VP, unable to undergo secondary bonding. The possible slowing of probe dynamics by hydrogen-bonding effects has been discussed[75] and demonstrated[76] previously via nonlinear optical studies investigating probe rotational dynamics in the presence of substantial probe−polymer secondary bonding. The effects are consistent[76] in magnitude with the slowing of the translational diffusion observed here for lophine in P2VP. Such effects of probe−polymer secondary interactions may even be apparent from comparisons of probe diffusion in PS and PiBMA. For the conditions tested, decacyclene has similar D values in the thicker PS and PiBMA films while lophine, which may undergo secondary bonding with polar ester groups, exhibits somewhat lower D values in thicker PiBMA films as compared to the thicker PS films.

The results presented in Figures 4, 6, and 7 indicate that, for the film thicknesses examined here, polymer−substrate affinity does not influence probe diffusion to a significant degree. This is evident given that the only system exhibiting substantial reductions in probe diffusion with decreasing thickness in ultrathin films is the PS system, which has no significant interactions with the substrate employed here. These results are consistent with those of Keddie et al.,[3] who found that polymer−substrate affinity played a role in ultrathin film T_g only for films thinner than 40 nm, which is below the film thickness range examined here. They are also consistent with studies of filled polymer systems, which indicate that specific energetic interactions between the polymer and filler play a minor role in volume relaxation and T_g behavior.[29]

To further study mobility near polymer−substrate and free surface interfaces, we modified our bilayer geometry to provide sensitivity to probe diffusion near a specific interface. Instead of the donor and acceptor layers being of equal film thickness as they are for the results shown in Figures 4, 6, and 7, we now make the donor layer much thinner than the acceptor layer. Placing this ultrathin donor layer at the substrate or free surface allows us to study probe diffusion toward the substrate or free surface interface without any competing effects from the opposite interface since the acceptor film will be of "bulk" dimensions (>200 nm thick). (This experiment differs from those reported in Figures 3−7 in that the latter experiments are specifically for *ultrathin* bilayer films while the former is done in a *thin* bilayer film geometry where the sensitivity to diffusion is limited to a region near the substrate or the polymer−air interface.) This experiment is similar to the studies of polymer diffusion near interfaces of Zheng et al.[36] and Lin et al.[37] except our small molecule probes are diffusing toward the interface instead of away from it.

Results of NRET studies of decacyclene diffusion toward the fused quartz substrate and toward the free surface are given in Figure 8 for donor layers as thin as 38 nm. Within experimental error, there is little

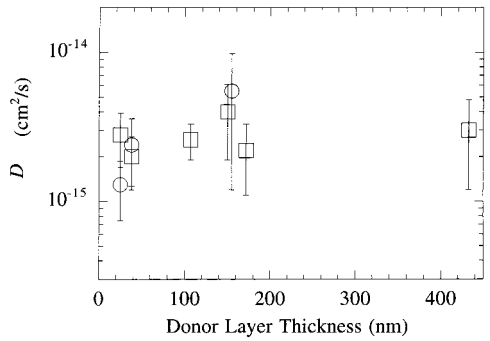

Figure 8. D as a function of donor-layer thickness with donor layer (○) at substrate and (□) at free surface for decacyclene diffusion in PS at 103 °C. (The acceptor layer thickness is >200 nm, meaning that the bilayer film is not ultrathin.)

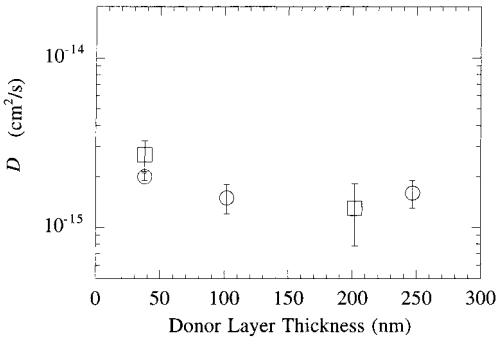

Figure 9. D as a function of donor-layer thickness with donor layer (○) at substrate and (□) at free surface for decacyclene diffusion in PiBMA at 69.5 °C. (The acceptor layer thickness is >200 nm, meaning that the bilayer film is not ultrathin.)

difference between probe diffusion toward the substrate interface or the free surface interface. Figure 9 shows results for the same experiment in PiBMA. Again, there is little difference between decacyclene diffusion toward the substrate or free surface for donor layers as thin as 38 nm. Diffusion into the thinnest interfacial layers of PiBMA may be slightly faster than the bulk, but there does not seem to be a dependence on whether the layer is at the substrate or free surface. The results shown in Figures 8 and 9 are consistent with the hypothesis that polymer−substrate affinity only affects the behavior of polymer chains in the immediate vicinity of the interface, <40 nm away. It also indicates that the effect of the free surface does not extend far into the film, consistent with most of the work involving this interface. (Our technique prohibits us from examining probe diffusion in substantially thinner layers.) The results for PS in Figure 8 do not show any slowing of probe diffusion as is found in Figure 4 for ultrathin films. This may appear contradictory if one assumes that the slowing of diffusion seen in the ultrathin films is due to the influence of the substrate interface. However, it is not clear at this time whether diffusion in an ultrathin film (Figure 4) and diffusion near an interface in a nonultrathin film (Figure 8), where chain confinement effects are less severe, are entirely analogous. This issue warrants further study.

Thus, the results in Figures 4 and 6−9 do not support the conclusion or interpretation by some that the influence of the polymer−substrate or polymer−free surface interactions on diffusion and polymer dynamics is long-range, up to 10−50 times R_g. It has been suggested that the slowing of polymer diffusion near a substrate could be interpreted through substantial

increases in T_g due to favorable polymer−substrate interactions.[36] However, if such an effect were present, it would be expected to be greater in systems with larger polymer−substrate interactions as the increase in T_g would be expected to be greater. Also, one would expect large differences in diffusion very close to a substrate as compared to far away from a substrate. Neither of these results is observed in Figures 4 and 6−9.

While it is clear from these studies that the role of polymer−substrate interactions on diffusive motion in polymer films must extend over only small distances (<40 nm), the cause of the apparent slowing of small molecule probe translational diffusion in PS ultrathin films remains to be explained. We know that it is not due to any strong affinity of PS for the fused quartz substrate since we have found no comparable drop in D for ultrathin films of stronger interacting polymer−substrate systems. Could it be due to an increase in T_g unrelated to polymer−substrate affinity? This is a potential explanation; however, it is not a very appealing one since techniques that measure T_g in a more direct manner[5,10] have indicated that, for the film thicknesses we have examined, T_g does not change measurably as compared to bulk.

Diffusion in polymers is influenced by many other considerations in addition to T_g. It is known that polymer chain conformation may be very different in ultrathin films and near interfaces than those found in the bulk state. In thin films, an extended chain conformation (as compared to the bulk) in the direction parallel to the interface has been predicted.[34] Changes in local chain conformation may then result in changes in the details of the breadth of the local cooperative segmental relaxation distribution. These may or may not be reflected in shifts in T_g (sensitive to the long-time side of the distribution) while nevertheless accommodating some change in probe diffusivity (sensitive to faster dynamics than is T_g). The magnitude of these effects may be substantially influenced by details of chain architecture (flexibility, number of available conformations) and also the nature of the interface (substrate, free surface, or polymer−polymer).

Additionally, the role of stress and strain in thin-film behavior has often been overlooked. Beaucage et al.[1] explained apparent T_g shifts in thin PS films on silicon wafers in terms of strains induced by cooling the films. It is well-known that mechanical stress and strain can change the properties of a polymer, including shifting T_g. Stress can be introduced during the film formation process (spin coating) or may be introduced during the heating or cooling of the film through a mismatch in the thermal expansion coefficient of the polymer and substrate. These types of stresses would become more important as film thickness is reduced. In our study, the bilayer films are heated quickly to temperatures above the bulk T_g of the polymer matrix, and then diffusion is measured at constant temperature. Since our measurements are above T_g, one may naively assume that the film is in an equilibrium state with negligible stress. However, the film is still constrained by the substrate, and only by removing the substrate may a chain fully relax to its unperturbed configuration and thus to a stress-free state. The magnitude and influence of these particular stress effects in determining ultrathin supported polymer film behavior are unclear. It could potentially explain the apparently contradictory results found in the literature for similar ultrathin film systems using different experimental techniques and thermal histories.

Clearly more work will be needed in order to understand fully the reasons for the observed effects of film thickness on probe and polymer diffusion in ultrathin PS films and the observed differences in the effect of thickness in ultrathin films of different polymers. In addition to the issues mentioned above, one issue unexplored in this study, but important in understanding the effect of film thickness on diffusion properties, concerns the effect of polymer molecular weight. Polymer molecular weight does not influence small molecule translational diffusion through bulk polymers (as long as molecular weight is large enough not to change T_g significantly) since it is coupled to polymer segmental mobility and not bulk chain diffusion. However, one may argue that due to chain connectivity, molecular weight could play a role in determining the film thickness at which deviations from bulk behavior are first observed. Effects of molecular weight in ultrathin PS films will be explored in the future along with issues regarding the impact of hydrogen and other secondary bonding between probe and polymer on the local cooperative segmental dynamics in the polymer and the rotational and translational dynamics of the probe.

Conclusions

The translational diffusivities of two small molecule probes have been measured in polymer films on quartz substrates as a function of film thickness using fluorescence NRET. Probe diffusion in PS films was found to slow as compared to bulk values when film thickness is decreased below approximately 150 nm. This result is qualitatively similar to that reported by Frank et al.[25] for lateral PS diffusion in ultrathin films. To determine whether such an effect is general and related to polymer−substrate interactions, studies of probe diffusion in PiBMA and P2VP ultrathin films were also undertaken. However, in PiBMA and P2VP, no discernible change in probe diffusion was found compared to bulk for films as thin as 50 and 88 nm, respectively. These results cannot be explained logically in terms of varying polymer−substrate affinity. (While not yet understood, these variable effects of film thickness may be related to chain packing in ultrathin supported films that is dependent on chain flexibility and architecture rather than polymer−substrate affinity.) Probe diffusion toward polymer−substrate interfaces and toward polymer−free surface interfaces has also been compared in PS and PiBMA films with little change in diffusion found in either geometry for interfacial layers as thin as 38 nm. These results are inconsistent with interpretations reached by Zheng et al.[36] regarding PS diffusion in similar geometries. However, these results, indicating that the range of influence of a particular polymer−free surface or polymer−substrate interaction does not extend very far (<40 nm) into thin and ultrathin films, are consistent with interpretations from T_g studies by Keddie et al.[3] and studies on PMMA diffusion by Lin et al.[37] which found the range of influence to be similarly small.

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References and Notes

(1) Beaucage, G.; Composto, R.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1993**, *31*, 319.
(2) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59.
(3) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Faraday Discuss.* **1994**, *98*, 219.
(4) Keddie, J. L.; Jones, R. A. L. *Isr. J. Chem.* **1995**, *35*, 21.
(5) Orts, W. J.; van Zanten, J. H.; Wu, W. L.; Satija, S. K. *Phys. Rev. Lett.* **1993**, *71*, 867.
(6) Wallace, W. E.; van Zanten, J. H.; Wu, W. L. *Phys. Rev. E* **1995**, *52*, R3329.
(7) Wu, W. L.; van Zanten, J. H.; Orts, W. J. *Macromolecules* **1995**, *28*, 771.
(8) van Zanten, J. H.; Wallace, W. E.; Wu, W. L. *Phys. Rev. E* **1996**, *53*, R2053.
(9) Forrest, J. A.; Dalnoki-Veress, K.; Dutcher, J. R. *Phys. Rev. Lett.* **1996**, *77*, 2002.
(10) Forrest, J. A.; Dalnoki-Veress, K.; Dutcher, J. R. *Phys. Rev. E* **1997**, *56*, 5705.
(11) Krausch, G.; Dai, C.-A.; Kramer, E. J.; Marko, J. F.; Bates, F. S. *Macromolecules* **1993**, *26*, 5566.
(12) Coulon, G.; Daillant, J.; Collin, B.; Benattar, J. J.; Gallot, Y. *Macromolecules* **1993**, *26*, 1582.
(13) Tang, H.; Szleifer, I.; Kumar, S. K. *J. Chem. Phys.* **1994**, *100*, 5367.
(14) Koneripalli, N.; Singh, N.; Levicky, R.; Bates, F. S.; Gallagher, P. D.; Satija, S. K. *Macromolecules* **1995**, *28*, 2897.
(15) Tanaka, K.; Yoon, J. S.; Takahara, A.; Kajiyama, T. *Macromolecules* **1995**, *28*, 934.
(16) Tanaka, K.; Takahara, A.; Kajiyama, T. *Macromolecules* **1996**, *29*, 3232.
(17) Despotopoulou, M. M.; Frank, C. W.; Miller, R. D.; Rabolt, J. F. *Macromolecules* **1996**, *29*, 5797.
(18) 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.
(19) Sutton, S. J.; Izumi, K.; Miyaji, H.; Miyamoto, Y.; Miyashita, S. *J. Mater. Sci.* **1997**, *32*, 5621.
(20) Srinivas, S.; Babu, J. R.; Riffle, J. S.; Wilkes, G. L. *J. Macromol. Sci., Phys.* **1997**, *B36*, 455.
(21) Despotopoulou, M. M.; Frank, C. W.; Miller, R. D.; Rabolt, J. F. *Macromolecules* **1995**, *28*, 6687.
(22) Grohens, Y.; Brogly, M.; Labbe, C.; Schultz, J. *Polymer* **1997**, *38*, 5913.
(23) Pfromm, P. H.; Koros, W. J. *Polymer* **1995**, *36*, 2379.
(24) Haas, C. K. Ph.D. Dissertation. Northwestern University, 1998.
(25) Frank, B.; Gast, A. P.; Russell, T. P.; Brown, H. R.; Hawker, C. *Macromolecules* **1996**, *29*, 6531.
(26) Reiter, G. *Europhys. Lett.* **1993**, *23*, 579.
(27) Reiter, G. *Macromolecules* **1994**, *27*, 3046.
(28) Hall, D. B.; Hooker, J. C.; Torkelson, J. M. *Macromolecules* **1997**, *30*, 667.
(29) Lipatov, Y. S.; Sergeeva, L. M. *Adsorption of Polymers*; Wiley: New York, 1974.
(30) Bitsanis, I.; Hadziioannou, G. *J. Chem. Phys.* **1990**, *92*, 3827.
(31) Mansfield, K. F.; Theodorou, D. N. *Macromolecules* **1991**, *24*, 6283.
(32) Mayes, A. M. *Macromolecules* **1994**, *27*, 3114.
(33) Baschnagel, J.; Binder, K. *Macromolecules* **1995**, *28*, 6808.
(34) Baschnagel, J.; Binder, K. *J. Phys. I* **1996**, *6*, 1271.
(35) Brown, H. R.; Russell, T. P. *Macromolecules* **1996**, *29*, 798.
(36) Zheng, X.; Rafailovich, M. H.; Sokolov, J.; Strzhemechny, Y.; Schwarz, S. A.; Sauer, B. B.; Rubinstein, M. *Phys. Rev. Lett.* **1997**, *79*, 241.
(37) Lin, E. K.; Wu, W. L.; Satija, S. K. *Macromolecules* **1997**, *30*, 7224.
(38) DeMaggio, G. B.; Frieze, W. E.; Gidley, D. W.; Zhu, M.; Hristov, H. A.; Yee, A. F. *Phys. Rev. Lett.* **1997**, *78*, 1524.
(39) Jean, Y. C.; Zhang, R.; Cao, H.; Yuan, J. P.; Huang, C. M. *Phys. Rev. B* **1997**, *56*, R8459.
(40) Meyers, G. F.; DeKoven, B. M.; Seitz, J. T. *Langmuir* **1992**, *8*, 2330.
(41) Kajiyama, T.; Tanaka, K.; Takahara, A. *Macromolecules* **1995**, *28*, 3482.
(42) Tanaka, K.; Taura, A.; Ge, S. R.; Takahara, A.; Kajiyama, T. *Macromolecules* **1996**, *29*, 3040.
(43) Kajiyama, T.; Tanaka, K.; Takahara, A. *Macromolecules* **1997**, *30*, 280.
(44) Tanaka, K.; Takahara, A.; Kajiyama, T. *Macromolecules* **1997**, *30*, 6626.
(45) Toney, M. F.; Russell, T. P.; Logan, J. A.; Kikuchi, H.; Sands, J. M.; Kumar, S. K. *Nature* **1995**, *374*, 709.
(46) Boiko, Y. M.; Prud'homme, R. E. *Macromolecules* **1997**, *30*, 3708.
(47) Boiko, Y. M.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1998**, *36*, 567.
(48) Liu, Y.; Russell, T. P.; Samant, M. G.; Stöhr, J.; Brown, H. R.; Cossy-Favre, A.; Diaz, J. *Macromolecules* **1997**, *30*, 7768.
(49) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1983.
(50) Berlman, I. B. *Energy Transfer Parameters of Aromatic Compounds*; Academic Press: New York, 1973.
(51) We have assumed that there is a homogeneous distribution of acceptor molecules throughout the acceptor layer prior to annealing. Small molecules may preferentially segregate to interfaces. This could potentially happen during the spin-coating process or by preferential diffusion toward an interface during annealing. One might expect that this type of effect could be exacerbated in ultrathin films potentially leading to changes in D with film thickness. However, we have no evidence, such as a substantial lag time for observed energy transfer (see Figures 3 and 5), that significant probe segregation is occurring in our films. The observed diffusive behavior with film thickness does not depend on probe type, and we also find little difference in diffusion whether the acceptor layer is next to the substrate or free surface in the bilayer geometry.
(52) Deppe, D. D.; Dhinojwala, A.; Torkelson, J. M. *Macromolecules* **1996**, *29*, 3898.
(53) In this analysis, we have assumed that κ^2, a factor describing the relative orientation of the donor and acceptor dipoles in space, is equal to $^2/_3$, the value for a random distribution of orientations. Assuming that donors or acceptors near surfaces may be initially oriented in some nonrandom manner, we must accept that this orientation will be randomized with any translational diffusion and therefore does not significantly affect energy-transfer efficiencies during diffusion. Furthermore, the exact value of κ^2 plays only a very minor role in the calculated diffusion coefficients, resulting in errors of less than 20% (well within the reported uncertainties) for a reasonably assumed range of κ^2 values. See ref 49 for a more extensive discussion related to κ^2 and NRET.
(54) Dhinojwala, A.; Torkelson, J. M. *Macromolecules* **1994**, *27*, 4817.
(55) Deppe, D. D. Ph.D. Dissertation, Northwestern University, 1996.
(56) Ho-Duc, N.; Daoust, H.; Gourdenne, A. *Polym. Prepr.* **1971**, *12* (1), 639.
(57) Hall, D. B.; Underhill, P.; Torkelson, J. M. *Polym. Eng. Sci.*, in press.
(58) P2VP may sorb significant amounts of water. Mass uptake and drying experiements on thick films indicated that our drying procedure removed, within error, all of the sorbed water. Any possible residual water that may have been present after the drying procedure was found not to shift T_g measurably, as determined by DSC measurements done on samples that experienced even harsher drying procedures.
(59) Hall, D. B.; Miller, R. D.; Torkelson, J. M. *J. Polym. Sci., Polym. Phys. Ed.* **1997**, *35*, 2795.
(60) Deppe, D. D.; Miller, R. D.; Torkelson, J. M. *J. Polym. Sci., Polym. Phys. Ed.* **1996**, *34*, 2987.
(61) Hall, D. B.; Deppe, D. D.; Hamilton, K. E.; Dhinojwala, A.; Torkelson, J. M. *J. Non-Cryst. Solids* **1998**, *235−237*, 48.
(62) Ehlich, D.; Sillescu, H. *Macromolecules* **1990**, *23*, 1600.
(63) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: London, 1980.
(64) Vrentas, J. S.; Duda, J. L. *J. Appl. Polym. Sci.* **1978**, *22*, 2325.
(65) Hadj Romdhane, I.; Danner, R. P.; Duda, J. L. *Ind. Eng. Chem. Res.* **1995**, *34*, 2833.
(66) Hall, D. B.; Dhinojwala, A.; Torkelson, J. M. *Phys. Rev. Lett.* **1997**, *79*, 103.
(67) Cicerone, M. T.; Blackburn, F. R.; Ediger, M. D. *Macromolecules* **1995**, *28*, 8224.
(68) Sillescu, H. *Phys. Rev. E* **1994**, *53*, 2992.
(69) Stillinger, F. H.; Hodgdon, J. A. *Phys. Rev. E* **1994**, *50*, 2064.

(70) Ediger, M. D. *J. Non-Cryst. Solids* **1998**, *235−237*, 10.
(71) Fujara, F.; Geil, B.; Sillescu, H.; Fleischer, G. *Z. Phys. B: Condens. Mater.* **1992**, *88*, 195.
(72) Probe volumes were estimated using the group contribution method of Sugden as reviewed by Haward (Haward, R. N *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *C42*, 191).
(73) Hall, D. B., unpublished results.
(74) Russell, T. P.; Kumar, S. K. *Nature* **1997**, *386*, 771.
(75) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Polym. Commun.* **1989**, *30*, 40.
(76) Hamilton, K. E. Ph.D. Dissertation, Northwestern University, 1996.

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