Mobility on Different Length Scales
in Thin Polymer Films

Connie B. Roth and John R. Dutcher*

*Polymer Surface & Interface Group, Department of Physics
and Centre for Food & Soft Materials Science,
University of Guelph, Ontario, Canada N1G 2W1*

October 24, 2003

Contents

---

*To whom correspondence should be addressed. Email: dutcher@physics.uoguelph.ca
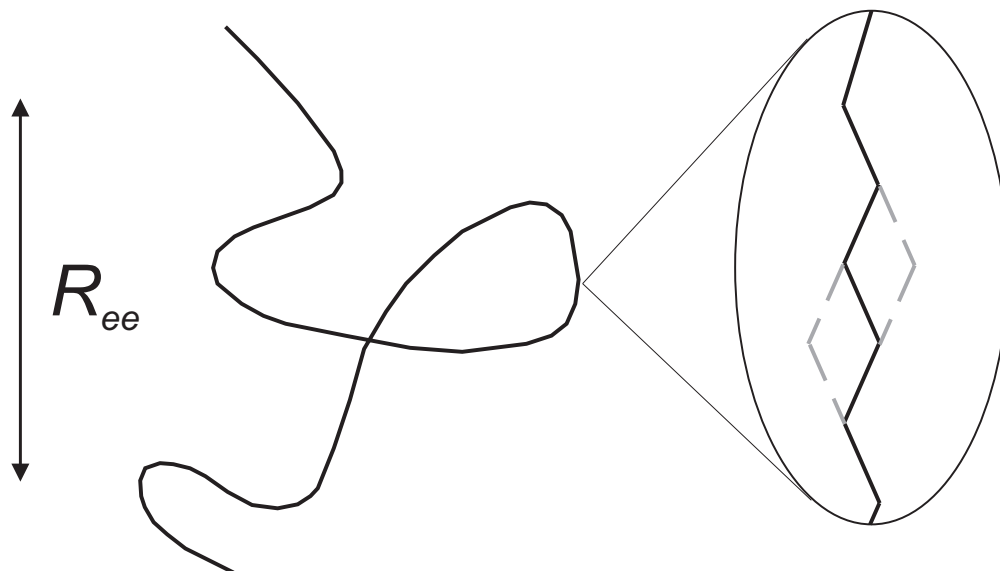
1

Figure 1: Schematic picture of a linear polymer molecule, including a magnification of a small number of segments of the molecule. The dashed lines indicate possible motions of the segments of the molecule.

1 Introduction

Thin polymer films with thicknesses of tens of nanometers are studied extensively both because they provide an ideal sample geometry for studying the effects of one-dimensional confinement on the structure, morphology and dynamics of the polymer molecules, and because they are used extensively in technological applications such as optical coatings, protective coatings, adhesives, barrier layers and packaging materials.

Polymer molecules can be prepared in a wide variety of different molecular architectures such as linear molecules, ring molecules, and branched molecules. The simplest molecular architecture corresponds to linear molecules that consist of identical monomer units connected end-to-end. In a collection of similar molecules, a linear polymer molecule will tend to form in the shape of a random coil. The overall coil size can be characterized statistically by the root-mean-square end-to-end distance R_{ee} which scales as the square root of the length of the molecule or its molecular weight M_w, and typically ranges from several nanometers to tens of nanometers. The polymer molecule can be described by a variety of different length scales, ranging from the size of the individual monomers to the overall size of the molecule R_{ee} (see Fig. 1). The corresponding time scales range from that corresponding to segmental relaxation, related to the glass transition, to that corresponding to the diffusion of entire chains.

In this chapter, we are concerned with the motion of polymer molecules confined to thin films. We begin by describing the basics of the motion of molecules on small length scales, which are related to the glass transition. This will be followed by discussions of mobility of polymer molecules on different length scales, and the effects of confinement on molecular motion on different length scales. The remainder of the chapter contains a detailed discussion of the experimental and theoretical studies of the dynamics of thin polymer films. General trends in the data are highlighted and outstanding issues are discussed.

1.1 The Glass Transition

In the simplest picture, the glass transition describes the transition from a rubber-like liquid to a glassy or amorphous solid as a material is cooled. The glass transition will occur upon cooling for almost any material, from organic liquids to metals to polymers, for a sufficiently fast cooling rate. To measure the glass transition temperature T_g, it is convenient to measure the volume or heat capacity as a function of temperature (see Fig. 2). Typically, one observes an abrupt change in the slope of the temperature dependence of the volume at
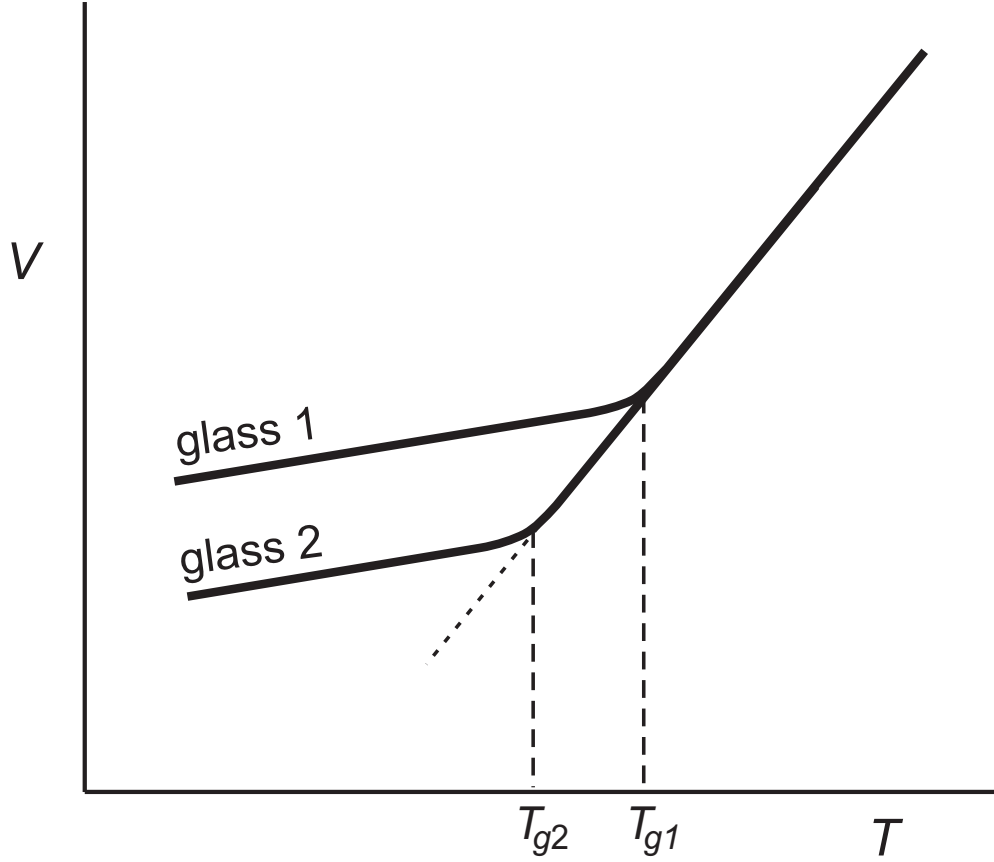
Figure 2: Volume V versus temperature T for a glass-forming material for two different cooling rates. Glass 1 has been cooled faster, resulting in a higher T_g value than that observed for the more slowly cooled glass 2.

a certain temperature which is identified as T_g. One also finds that the glass transition temperature measured in such an experiment depends on the cooling or heating rate (see Fig. 2), as well as on the thermal history of the sample. A sample which is cooled faster falls out of equilibrium at a higher temperature, resulting in a T_g value that is higher than that observed for a slower cooling rate.

Because of the dependence of T_g on time, the glass transition is not a true thermodynamic phase transition, but rather it is a kinetic transition in which the motion of the molecules is slowed so dramatically upon cooling that, at sufficiently low temperatures, no appreciable motion of the molecules can occur. The slowing of the dynamics upon cooling can be observed directly by a dramatic increase in the viscosity of the liquid. For example, the viscosity of o-terphenyl, a simple glass-former, increases by nine orders of magnitude in the 30°C temperature range above T_g [1]. Unlike the large structural changes observed during the formation of a crystal upon cooling, only very subtle structural changes are observed during the formation of a glass, with the structure of the high temperature liquid effectively frozen in with rapid cooling.

We can understand the frequency (or time) dependence of the measured T_g values if we consider structural relaxation of the material near T_g. If we consider a simplified material that has a single characteristic relaxation time τ at a given temperature, then for short times or correspondingly high frequencies, no significant structural relaxation can occur during the experiment so that the material appears to be solid-like. For times that are much longer than τ or correspondingly low frequencies, the material fully relaxes during the experiment so that the material appears to be liquid-like. If τ increases strongly with decreasing temperature, then below a certain temperature, relaxation for that mobility mode is effectively frozen. For a glass-forming material, physical quantities such as volume or index of refraction will relax in response to a
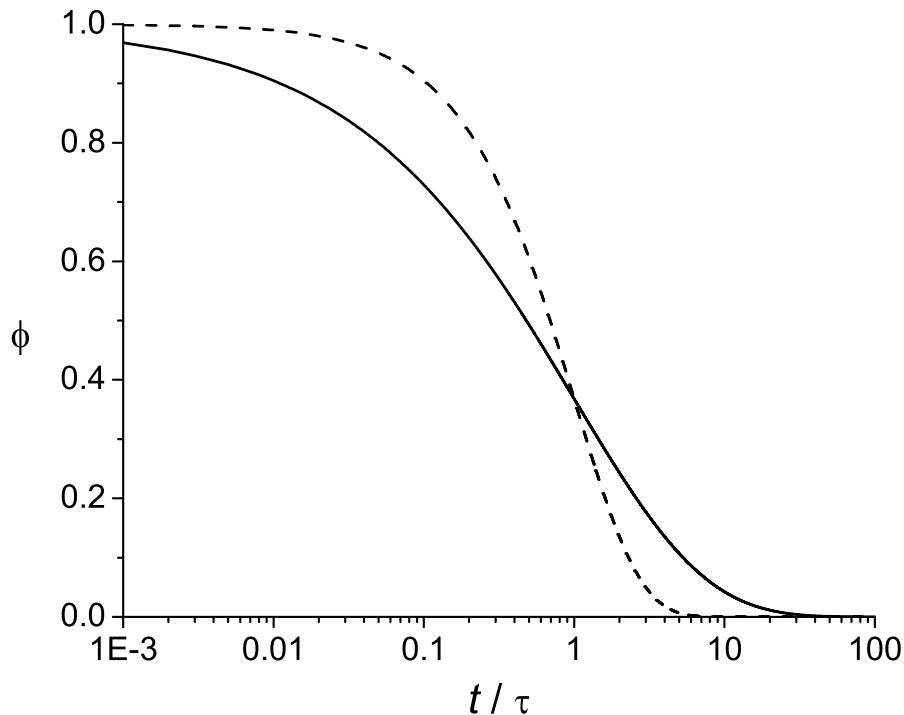
Figure 3: Relaxation function ϕ versus t/τ for an idealized glass-forming material characterized by a single relaxation time τ. The solid line corresponds to $\beta = 0.5$ (stretched exponential) and the dashed line corresponds to $\beta = 1$.

change in an experimental parameter such as temperature. At a given temperature, the relaxation function $\phi(t)$ can be described by a so-called stretched exponential (Kohlrausch-Williams-Watt or KWW) function:

$$\phi(t) \sim \exp[-(t/\tau)^{\beta}]. \qquad (1)$$

The relaxation function is shown schematically as a plot of ϕ versus t/τ in Fig. 3 for two different values of β. For $\beta = 1$, the decay is a single exponential; for $\beta < 1$, which is typical for glass-forming materials, the decay is nonexponential and is "stretched" in time compared with the exponential decay. The nonexponential behaviour has two possible explanations: either the sample is homogeneous, with each molecule obeying the same nonexponential relaxation; or the sample is dynamically heterogeneous, consisting of regions with different dynamics, each obeying nearly exponential relaxation, with different regions having significantly different relaxation times. For a recent review summarizing the experimental evidence supporting dynamic heterogeneity, see Ref. [2].

As mentioned above, cooling of a glass-forming liquid makes it progressively more difficult for the molecules to move significantly on the experimental time scale. This dramatic slowing of the dynamics is difficult to understand theoretically [2, 3]. There have been a number of different theoretical approaches to attempt to understand the glass transition, including free volume, cooperative motion and mode coupling theories. Despite these impressive efforts, no complete theory of the glass transition exists today; for a recent discussion of the relevant issues, see Refs. [3, 4]. However, there are two simple concepts that have been useful in trying to explain the dramatic reduction in molecular mobility with decreasing temperature. The basic ideas of the free volume and cooperative motion theories are quite simple. The motion of individual particles in a glass-forming material requires sufficient free volume into which the particles can move. As the temperature is decreased, the density increases and it becomes increasingly difficult for a particle to find sufficient free volume for motion to occur on a reasonable time scale [5]. One way to achieve motion at low

4

temperatures is to allow a cooperative rearrangement of neighbouring particles such that many particles must move together if *any* motion is to occur at all. Adam and Gibbs postulated the existence of cooperatively rearranging regions or CRRs as the smallest regions at a given temperature that can rearrange independent of neighbouring regions [6]. In their theory, the size of the CRRs was inversely related to the configurational entropy of the system, such that the CRR size increased with decreasing temperature. Experiments indicate that the size of these regions is several nanometers [7, 8]. Although the CRRs were originally envisioned as spherical volumes of diameter ξ, recent computer simulations have shown that the cooperative motion is essentially string-like [9], with the average string length increasing with decreasing temperature. A shortcoming of the Adam-Gibbs approach is the assumption of no interaction between neighbouring regions. Because the string-like shape is less compact than the spherical shape, interaction between neighbouring regions will be more significant and this could have a distinctive signature for the effect of confinement on the dynamic properties of glass-forming liquids.

1.2 Motion of Polymer Molecules on Different Length Scales in Bulk Samples

For polymer molecules, motion can occur on a variety of length scales, from the relaxation of molecular segments, as discussed in the previous section, to diffusion of entire chains. There will be a range of characteristic times at a given temperature corresponding to motion at different length scales, with longer times characterizing motion on larger length scales. If one cools a sample at a certain rate, the mobility modes corresponding to longer relaxation times will freeze out before the mobility modes corresponding to shorter relaxation times. Despite the large difference in the length scale and character of the different motions of a molecule, the temperature dependence of the viscosity, characterizing whole chain diffusion, is typically very similar to that for the characteristic times corresponding to the glass transition (α-relaxation). Specifically, the temperature dependence of the viscosity and the α-relaxation times is well-described by a Vogel-Fulcher function of the form

$$A \exp[T_A/(T - T_0)] \tag{2}$$

with similar values of T_A and T_0. In Eq. 2, T_A is an "activation temperature", T_0 is the temperature at which the exponential factor diverges to infinity (typically $T_g - 50$ K for polymers), and A is a temperature-independent prefactor. The similarity of the temperature dependence of dynamic processes that occur on different length scales is a phenomenon known as thermorheological simplicity, and it is the basis for time-temperature superposition which is used extensively in the study of the mechanical properties of bulk polymers [10, 11]. A schematic diagram of the time dependence of the compliance $J(t)$ of a bulk linear polymer is shown for two temperatures in Fig. 4 (for a detailed description of $J(t)$, see e.g. Ref. [10]). The $J(t)$ curve contains regions corresponding to the glass transition (B) and terminal flow or chain diffusion (D) that are separated in time because of the presence of the rubber plateau (C) for high molecular weight polymers. Time-temperature superposition means that a change in temperature produces equal shifts in time for the different regions of the $J(t)$ curve. In practice, because the $J(t)$ curve spans many orders of magnitude in time, the complete curve is typically obtained by performing measurements over a limited range of times at different temperatures and shifting the different curves in time using the principle of time-temperature superposition. Although there are deviations from thermorheological simplicity for most polymers, the deviations are typically small and the principle of time-temperature superposition holds reasonably well [12]. It has been suggested that the origin of the similar temperature dependence for motion of polymer molecules at different length scales is related to a property of the individual segments, e.g. segmental frictional force [10].

1.3 Effects of Confinement on Motion of Polymer Molecules

The idea of observing changes to the dynamics of molecules by confining them to dimensions comparable to that over which motion occurs is appealing. For example, the possible existence of the cooperativity length scale in the Adam-Gibbs theory allows for the possibility of observing so-called finite size effects in which the size of the sample becomes comparable to the cooperativity length scale as the temperature is varied. Will the mobility of the molecules increase or decrease upon confinement? Imagine a collection of molecules confined to a channel with a diameter d which is on the nanometer length scale. Upon cooling, the cooperativity length scale can become larger than the diameter of the channel. Based on the Adam-Gibbs model, the effect of confinement is to decrease the entropy which should lead to a slowing down of
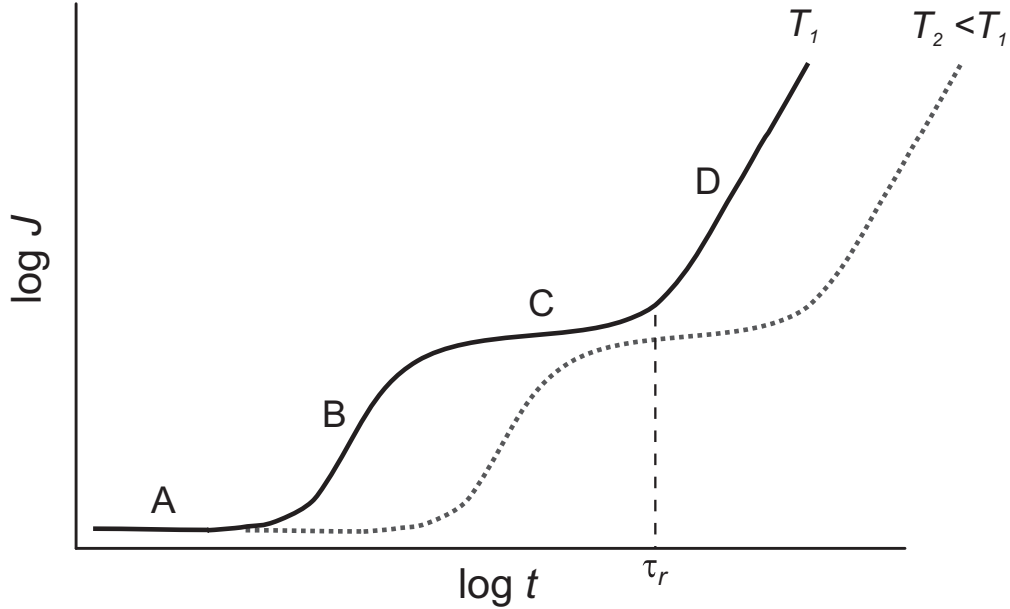
Figure 4: Compliance J versus time t for a bulk linear polymer. Various regions of the compliance curve are labelled. A: glassy plateau; B: glass-rubber transition; C: rubber plateau; and D: terminal flow region. The reptation time τ_r for the solid curve is indicated by the vertical dashed line.

the dynamics and an increase in T_g. However, the nature of the bounding surface will have a large effect. If there is a large attractive interaction between the molecules and the bounding surface, the mobility will decrease, whereas if the molecules at the bounding surface can move more freely, as is the case of a free or neutral surface, then the overall mobility will increase.

The effect of confinement on molecular mobility has focused either on measurements of simple liquids confined in rather complicated geometries such as porous glasses or measurements of more complex molecules such as polymers confined in simple confining geometries such as thin films. Each type of study can contribute to the overall understanding of the effects of confinement on molecular mobility, but, as will become clear in the discussion below, the results have to be examined carefully to reconcile the measurements with existing and new theories and to resolve apparent contradictions between different measurements on the same and different molecular systems. The picture that emerges is quite coherent, albeit with several surprises and unexplained results.

Finite size effects on T_g were first observed by Jackson and McKenna for simple liquids confined within porous glasses, which had pore diameters on the nanometer scale [13]. They used differential scanning calorimetry (DSC) to measure T_g in these systems. Contrary to their initial expectations based on the Adam-Gibbs theory, they observed reductions in T_g, indicating an increase in mobility, as the pore size was decreased. This original work of Jackson and McKenna has led to extensive experimental and theoretical studies of the effects of confinement on the glass transition using a variety of different sample geometries and different molecules (see, for example, Ref. [14]).

By confining polymer molecules to dimensions that are comparable to the different length scales characterizing the molecules, the motion of the molecules can be significantly different than in bulk. Considerable evidence has been obtained that the glass transition temperature T_g of thin polymer films can be substantially different from that in bulk (see, for example, Refs. [15, 16, 17]). The effect of confinement on the segmental motion of polymers has been studied using a variety of experimental geometries: interfaces in semicrystalline polymers [18], polymer solutions in porous glasses [19], polymers intercalated into the 2 nm gaps of layered compounds [20], polymer spheres with diameters of tens of nanometers [21], and thin polymer films. We will focus on results obtained for polymer molecules confined to thin films. The simple thin film geometry is appealing since it is straightforward to control the interactions at the free surface and film-substrate in-

terface, and it is possible to produce films of uniform thickness, and therefore uniform confinement, which can be varied continuously from nanometers to micrometers. In this way, it is possible to probe both chain confinement effects, in which the film thickness is comparable to the overall size of the molecule, as well as finite size effects.

In contrast to the confinement-induced changes in T_g, it has been found that whole chain motion in thin polymer films is not substantially different from that in bulk, as discussed below. The reconciliation of confinement-induced changes to the segmental mobility with no corresponding changes to whole chain diffusion requires the introduction of concepts that are particular to confined systems, such as spatial gradients in molecular mobility near a free surface or interface, or the invalidity of bulk concepts such as time-temperature superposition. In this chapter, we will review recent experimental, theoretical and computational studies of the effects on the mobility of polymer molecules of confinement to thin films. It is our hope that this critical discussion of the studies to date will lead to a greater understanding of this complex problem.

2 Experimental studies

To probe the molecular mobility in thin polymer films, it is necessary to use a technique that has high sensitivity, because of the small sample volume, or surface sensitivity, which is advantageous because of the large surface-to-volume ratio in thin films. In general, traditional techniques used to probe the glass transition and chain diffusion in bulk samples, e.g. differential scanning calorimetry and neutron scattering, do not have sufficient sensitivity. It is possible to prepare and measure stacks of identical films using bulk techniques [22], but the requirements for sample preparation are very demanding. Instead, new techniques have been developed and existing techniques have been used and adapted to obtain measures of the molecular mobility on different length scales in thin polymer films and at free surfaces of polymers.

2.1 Glass transition in thin polymer films

2.1.1 Supported films

The first systematic study of the dependence of the glass transition temperature T_g on film thickness in thin polymer films was performed by Keddie *et al.* using ellipsometry [23]. In the ellipsometry experiment, the measured change in polarization of light upon reflection from or transmission through the polymer film is used to obtain the thickness h and index of refraction n of the film. To measure the glass transition temperature, the film thickness is measured as a function of temperature, and the temperature corresponding to the near discontinuous change in the thermal expansion (see Fig. 2) is identified as T_g. Keddie *et al.* prepared a series of polystyrene (PS) films on the native oxide layer of silicon wafers with film thicknesses $10 \, \text{nm} < h < 200 \, \text{nm}$ and molecular weights $120 \times 10^3 < M_w < 2900 \times 10^3$. They measured reductions in T_g for $h < 40 \, \text{nm}$, with quantitatively similar results for all M_w values. The data were fitted to an empirical function based on the assumption of the existence of a liquid-like layer at the free surface of the film:

$$T_g(h) = T_g^{\text{bulk}} \left[1 - \left(\frac{\alpha}{h} \right)^{\delta} \right], \tag{3}$$

where $\alpha = 3.2 \, \text{nm}$ and $\delta = 1.8$. A compilation of results obtained for PS films on a variety of substrates using numerous experimental techniques such as ellipsometry [23, 24, 25, 26, 27], dielectric spectroscopy [28, 29], x-ray reflectivity [30], positron annihilation lifetime spectroscopy (PALS) [31], local thermal analysis [32] and probe fluorescence intensity [33, 34, 35] is shown in Fig. 5. The trend in the data shown in Fig. 5 is clear: there is a decrease in T_g with decreasing film thickness for all of the data, with good quantitative agreement between data obtained using the different techniques. Since similar results are obtained for PS films on different substrates, one can conclude that the PS films interact only weakly with the underlying substrates. This is not always the case. The importance of the effect of the polymer-substrate interaction on the measured T_g value was first observed for the case of poly (methyl methacrylate) (PMMA) films on Au surfaces and the native silicon oxide layer of silicon wafers. T_g decreased with decreasing film thickness for PMMA films on Au, but a modest increase in T_g was observed with decreasing film thickness for PMMA films on silicon oxide [36]. Subsequently, evidence for a strongly attractive interaction between the polymer and
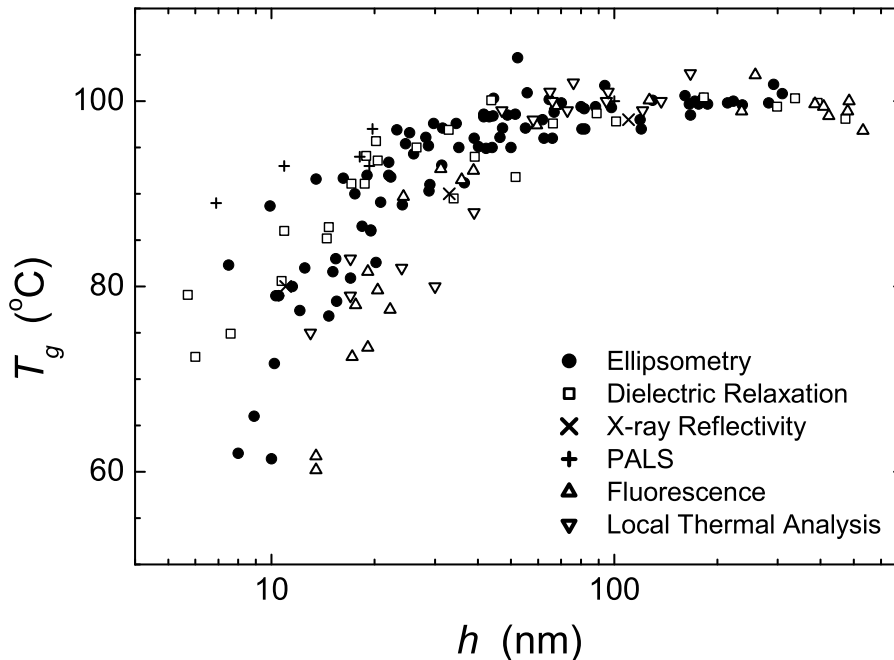
Figure 5: Glass transition temperature T_g as a function of film thickness h measured for polystyrene (PS) of different molecular weights M_w supported on a variety of substrates using six different techniques: ellipsometry [23, 24, 25, 26, 27], dielectric relaxation [29], x-ray reflectivity [30], positron annihilation lifetime spectroscopy (PALS) [31], fluorescence intensity [35], and local thermal analysis [32]. Note: The data from Refs. [24, 29] have been shifted in temperature by $+3°C$ so that the bulk T_g values match for all datasets.

underlying substrate was observed in x-ray reflectivity measurements of poly-(2)-vinylpyridine on a silicon oxide layer on silicon as an increase in T_g with decreasing thickness [37].

As can be seen from the data presented in Fig. 5, there are several different experimental techniques that have been used to measure T_g in supported thin polymer films. All of these techniques probe the material properties averaged across the thickness of the film, yielding an average T_g value for the film. However, it is important to determine whether each of these techniques measures the same physical quantity, e.g. is the T_g value measured by ellipsometry and dielectric relaxation (DR) the same physical quantity? Recent DR measurements of isotactic PMMA sandwiched between Al electrodes [38] and ellipsometry measurements of isotactic PMMA on Al substrates [39] show at least qualitative agreement between the T_g values determined using both techniques. Such comparisons are important for a proper discussion of T_g results obtained using different experimental techniques.

The determination of T_g becomes more difficult as the film thickness is decreased for several reasons: (1) there is a reduction in signal strength because less material is being probed in the experiment; (2) there is a reduction in the contrast between the slopes characterizing the glass and melt regions; and (3) there is a broadening of the transition [27]. Items (2) and (3) have been shown to be consistent with the presence of a thin liquid-like layer at the free surface [27]. Despite these effects which make the determination of T_g difficult, T_g values have been obtained for films with thicknesses as small as 6 nm (see Fig. 5).

The presence of the film surfaces creates environments for the polymer segments in contact with the surface that differ from that of segments within the film. In particular, it is reasonable to expect that segments in contact with a free surface are more mobile. Most theoretical models that have been proposed to explain T_g reductions in very thin polymer films begin with this premise and account for variations in segmental mobility across the film thickness as well as novel mechanisms by which the enhanced mobility

near the free surface can be transferred deeper into the film [40].

Recently, it has been suggested that attention should be focused on measurements of the distribution of T_g values across the thickness of the film [40, 41], rather than measurements of the average T_g value. In response to this suggestion, Ellison and Torkelson have applied the probe fluorescence technique [33, 34] to multilayer films incorporating thin layers which contain small quantities of fluorescent probes (either probe molecules or probe-labeled polymer molecules) [35]. The authors have verified that the temperature dependence of the fluorescence intensity provided a measure of the temperature dependence of the density and therefore the T_g value of the film, and that there is not substantial segregation of the probe molecules to one or both film surfaces. By using the multilayer geometry and varying the position of the fluorescently-tagged layer within the film, the authors were able to obtain the distribution of T_g values across the thickness of the film. They found a decrease in T_g near a free surface which extends several tens of nanometers into the film [35]. This large length scale for the effect of the free surface on T_g is considerably larger than that inferred from other measurements on polymer films [27, 42] and for other systems using other techniques (see below) which have been interpreted in terms of models with layers of different mobility based on measurements of average T_g values. In addition, Ellison and Torkelson have shown that the magnitude of the reduction in T_g at the free surface can also depend on the overall thickness of the film for films with thicknesses less than the spatial extent of the enhanced mobility at a free surface.

Several studies have focused on measuring the distribution of α-relaxation times in thin polymer films, using the techniques of second harmonic generation (SHG) [43] and dielectric relaxation (DR) spectroscopy [28, 29, 38, 44, 45, 46]. These studies have allowed a detailed determination of the α-relaxation time distribution in the films. The SHG experiments, performed on a copolymer of isobutyl methacrylate and dye-functionalized methacrylate monomer, revealed no change in the average α-relaxation time with decreasing film thickness, with a corresponding broadening of the α-relaxation time distribution with decreasing film thickness. However, the interaction between the large amounts of dye labels and the substrate may have caused the invariance of the average α-relaxation time with film thickness [34]. DR spectroscopy was used by Fukao to study thin films of PS, poly(vinyl acetate) and atactic PMMA [28, 29, 44]. For the PS films, the glass transition temperature was identified as the discontinuous change in the temperature dependence of the capacitance which is determined by the thermal expansion of the polymer film [28]. T_g values determined in this manner decreased with decreasing film thickness in agreement with the results of other techniques (see Fig. 5). The average α-relaxation temperature T_α was observed to decrease with decreasing film thickness but only below a threshold film thickness value that was small compared with film thicknesses for which T_g reductions were observed using other techniques. In addition, the width of the α-relaxation peak ΔT_α was observed to broaden with decreasing film thickness. Subsequent DR measurements of isotactic PMMA (i-PMMA), which has a large dielectric α-relaxation signal, revealed a decrease in T_g with decreasing film thickness, together with a broadening of the relaxation time distribution and a reduction in the dielectric strength for the α-relaxation process [38]. In this study, the temperature dependence of the relaxation time corresponding to the maximum in the α-relaxation loss peak was fitted to Eq. 2 and T_g was identified as the temperature at which the relaxation time was equal to 100 s. The multilayer film geometry has also been used recently in dielectric relaxation studies of polymer trilayer films consisting of a dielectrically active layer (i-PMMA) sandwiched between two layers of a different polymer (PS) [46]. T_g values for the i-PMMA layers were determined by applying an activation energy fine-structure analysis [47] to the dielectric data. A slight increase in T_g with decreasing i-PMMA film thickness was observed, which is qualitatively different from the decrease in T_g with decreasing film thickness observed for the same i-PMMA films in contact with the metallic electrodes. Dielectric relaxation measurements of i-PMMA films with one free surface have shown that the α-process measured at 1 kHz was the same with and without the electrode in contact with the top surface of the polymer film for film thicknesses down to 7 nm [39]. This result is consistent with previous studies that have shown that the presence of thin capping layers on polymer films have no measurable effect on the $T_g(h)$ dynamics [24].

2.1.2   Freely-standing films

The experimental data obtained for polymer films supported on substrates indicate that the presence of the free surface tends to decrease T_g, whereas the presence of the underlying substrate can tend to increase T_g. The T_g value measured for a particular polymer-substrate combination will depend on which film interface
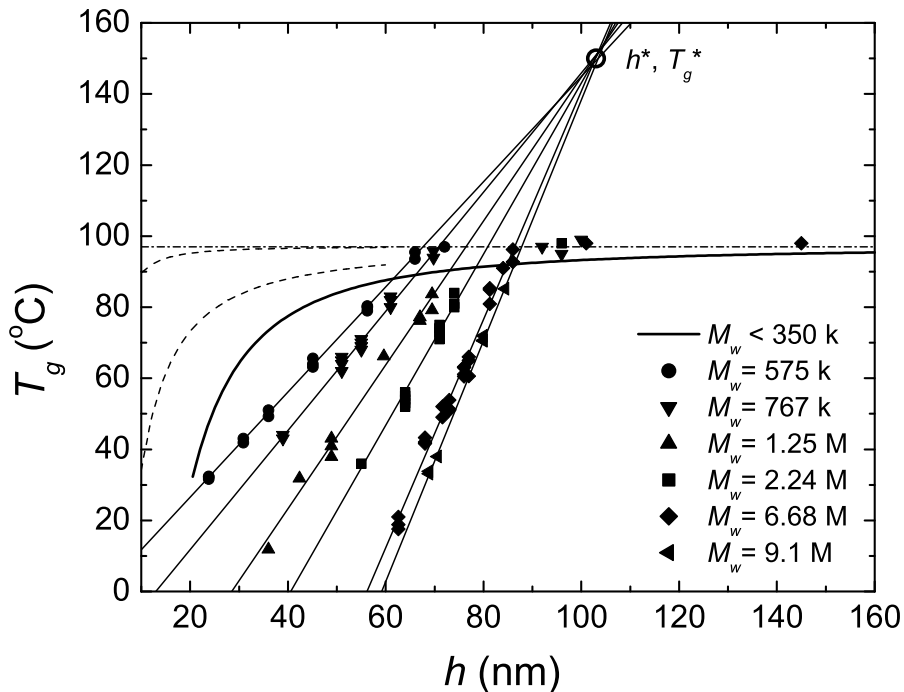
Figure 6: Glass transition temperature T_g as a function of film thickness h for freely-standing polystyrene films of different molecular weights. High M_w data, measured using ellipsometry, are displayed using a different symbol for each M_w value [51], and data for $M_w < 350 \times 10^3$, measured using Brillouin light scattering, are indicated by the thick solid line [50]. The dashed lines for $h < 60$ nm represent the spread and uncertainty in the T_g data obtained for supported PS films (see Fig. 5). The small circle indicates the common intersection point (h^*, T_g^*) of the straight line fits to the reduced T_g data for the high M_w films.

dominates. To clarify the role of the free surface on the measured T_g value, the underlying substrate was removed and freely-standing polymer films, with air-polymer interfaces on both sides of the film, were studied [24, 48, 49, 50, 51, 52]. Data points obtained using transmission ellipsometry for freely-standing films of narrow distribution PS for different M_w values within the range $575 \times 10^3 < M_w < 9100 \times 10^3$ are indicated with symbols in Fig. 6 [51]. The T_g values obtained using transmission ellipsometry are the same to within experimental uncertainty as the T_g values measured using Brillouin light scattering (BLS) in the original measurements of freely-standing PS films [24, 48]. This is particularly significant since the two techniques measure different physical properties of the films: BLS measures the light scattering from the rippling of the film surfaces due to thermally-excited, film-guided acoustic phonons and is insensitive to film thickness, whereas the ellipsometry signal is determined by multiple reflections of light from the two film surfaces and yields a measure of the film thickness [53]. Because the BLS signal is determined by the surface ripple, the signal strength does not decrease with decreasing film thickness, unlike all of the other experimental techniques that have been used to probe the glass transition in freely-standing polymer films.

The most striking feature of the data presented in Fig. 6 is that the T_g reductions are much larger for freely-standing films than they are for supported films. The data obtained for each M_w value has the same qualitative dependence on film thickness h: a constant T_g value equal to that in bulk for sufficiently thick films, and a linear reduction in T_g with h for h less than a threshold film thickness value h_0. This dependence of T_g on h can be interpreted as the interplay between two types of mobility: the bulk mechanism which dominates for sufficiently thick films, and a new mode of mobility which becomes more efficient than the
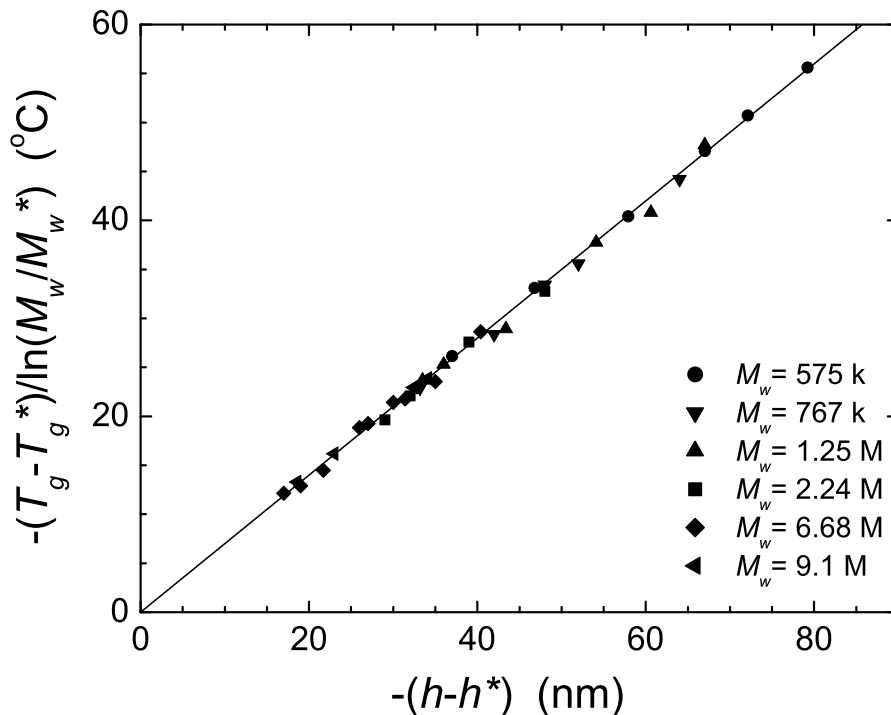
Figure 7: Scaling plot of all of the reduced T_g values for all molecular weights and film thicknesses for the data shown in Fig. 6.

bulk mechanism for sufficiently thin films, resulting in reduced T_g values [40]. de Gennes has suggested a mechanism for propagating the mobility of the near-surface segments to depths comparable to the overall size of the polymer molecules, which could give rise to T_g reductions over length scales comparable to the overall size of the polymer molecules [40].

For the $T_g(h)$ data in Fig. 6, there is also a systematic dependence on M_w: an increase in the slope of T_g versus h and the threshold film thickness value h_0 with increasing M_w. The dependence of the $T_g(h)$ data on M_w, or equivalently the overall size of the molecules, is unexpected because the glass transition is associated with motion on a much smaller, segmental length scale and also because the $T_g(h)$ data obtained for supported polymer films show no measurable dependence on M_w [23, 26]. This so-called chain confinement effect, in which deviations from bulk behaviour are dependent on the overall size of the polymer molecules, is unique to high M_w freely-standing PS films. The freely-standing PS film data is even more remarkable if one fits the film thickness dependence of the reduced T_g data for each M_w value and extrapolates the straight line fits to larger temperature: all six of the straight lines, one for each M_w value, intersect at a single point (h^*, T_g^*) [51, 54]. The existence of the intersection point means that, by empirically accounting for the M_w-dependence, all of the reduced T_g values in Fig. 6 can be replotted as a universal scaling plot, as shown in Fig. 7. The collapse of all of the data onto a single line is remarkable. However, the physical significance of the intersection point is not yet understood. To determine if the remarkable scaling behaviour shown in Fig. 6 is specific to PS or is more general, measurements have begun on freely-standing films of another polymer, poly (methyl methacrylate) (PMMA). T_g measurements on freely-standing films of atactic PMMA (a-PMMA) of a single M_w value have been reported [52]. A comparison of the $T_g(h)$ data obtained for freely-standing PS and a-PMMA films of nearly equivalent M_w values is shown in Fig. 8. The same qualitative dependence of T_g on h is observed for both data sets, but the magnitude of the T_g reductions at a given film thickness below the threshold film thickness value is substantially less for the a-PMMA films than for the PS films. This indicates that theoretical models which are proposed to explain T_g reductions in
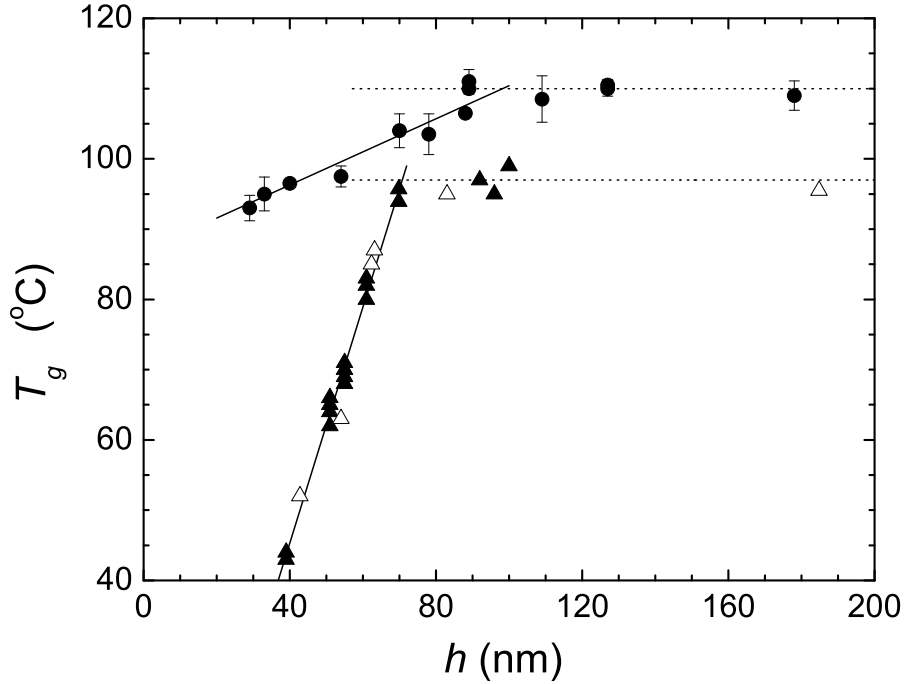
11

Figure 8: Comparison of $T_g(h)$ results for freely-standing PS films (solid triangles: ellipsometry [51]; open triangles: Brillouin light scattering [24]) and PMMA films (solid circles: ellipsometry [52]) of nearly equivalent molecular weights: $M_w = 767 \times 10^3$ for PS and $M_w = 790 \times 10^3$ for a-PMMA.

freely-standing polymer films will need to account for polymer-specific properties, e.g. chemical structure or steric hindrance.

Measurements performed on films with $M_w < 350 \times 10^3$ (low M_w) have revealed T_g reductions with decreasing film thickness that are comparable in absolute terms to those observed with larger M_w values, but there is no significant M_w-dependence of the $T_g(h)$ behaviour for the low M_w films (see the solid curve in Fig. 6) [50]. The lack of M_w-dependence of the T_g reductions observed for the low M_w values is reminiscent of the behaviour observed for supported polymer films. In fact, the T_g reductions for low M_w freely-standing polymer films are essentially twice as large as those observed for supported polymer films, suggesting that the magnitude of the T_g reduction scales with the number of free surfaces [42]. The low M_w freely-standing polymer film experimental results have been interpreted in terms of a three layer model in which the layers at the free surfaces are assumed to be more mobile, and the results are consistent with free surface layers which have temperature dependent thicknesses that scale with temperature in the same manner as the cooperativity length scale [42].

There are several intriguing aspects to the T_g data obtained for freely-standing polymer films. First, the existence of the common intersection point on the plot of T_g versus h for films with different, large M_w values (see Fig. 6) is striking, but its significance is not yet known. Second, the crossover between a M_w-dependence for high M_w films, indicative of chain confinement effects, and a lack of M_w-dependence for low M_w films is not understood. Third, the glass transition observed with both BLS and ellipsometry is very sharp (only several °C) for all film thicknesses, whereas one would expect that the existence of more mobile surface layers would produce a broadening of the transition for very thin films. All of these aspects of the freely-standing polymer film T_g results are intriguing and deserve more careful study.

Recently, T_g measurements have been performed using differential scanning calorimetry (DSC) of aqueous suspensions of PS spheres with diameters of tens of nanometers [21]. It is reasonable to compare these

12

results with those obtained for freely-standing polymer films because the spheres in aqueous suspension in the absence of aggregation are in contact only with water and therefore are essentially unsupported. By placing many spheres in the suspension, while taking care to avoid aggregation, it was possible to obtain sufficient signal using differential scanning calorimetry (DSC), a technique that is commonly used to measure T_g in bulk samples. In this study, the jump in the specific heat associated with the transition was observed to decrease with decreasing sphere diameter, and these results were interpreted in terms of a central core with bulk dynamics and an outer shell of 4 nm thickness with faster dynamics. The measured T_g values were not substantially less than the bulk value, in contrast to the large T_g reductions obtained for freely-standing PS films. In comparing the results of this study with those obtained for freely-standing films, it is important to note two important differences: (1) The PS spheres were produced by microemulsion polymerization in the presence of small quantities of surfactant molecules (to stabilize the spheres in suspension) and therefore have larger polydispersity, different surface character and less chain orientation than for spincoated PS freely-standing films; (2) The nature of the confinement is different and this has implications for the equilibration of the samples. Obviously, there is a qualitative difference in the confinement of the polymer molecules: within the spheres, the polymer molecules are confined in three dimensions, instead of the one-dimensional confinement produced in very thin polymer films. The sphere geometry is appealing since it is an equilibrium shape that minimizes the surface-area-to-volume ratio. This allows the spheres to be heated above the bulk T_g value without the instabilities that are inherent to thin polymer films (see below).

There have been only preliminary attempts to measure the relaxation dynamics of freely-standing PS films [22, 55]. A photon correlation spectroscopy (PCS) study revealed a dramatic increase in the relaxation within a 22 nm thick PS film as the temperature was increased modestly in a small range around room temperature, corresponding to temperatures comparable to the T_g value measured using BLS [55]. The PCS data were well described by a stretched exponential function (Eq. 1) with a β value that was indistinguishable from that in bulk PS. Inelastic neutron scattering measurements have been performed on stacks of a large number of identical freely-standing PS films with a total film thickness of approximately 7.5 μm [22]. Although these measurements were at the edge of feasibility, a small but measurable enhancement of the mean-square-displacements, and therefore faster dynamics, was observed for a sample consisting of a stack of 140 films, each of 55 nm thickness.

2.2   Whole chain motion in thin polymer films

The first indication of enhanced mobility in thin polymer films was inferred from optical microscopy studies by Reiter of the breakup or dewetting of thin polymer films at temperatures less than the bulk value of T_g [56]. These measurements necessarily involve motion of entire polymer molecules due to the formation and growth of holes in the films. Subsequent measurements of whole chain mobility in thin polymer films have focused on diffusion using fluorescently tagged probe and polymer molecules, diffusion at interfaces between two films, and detailed studies of dewetting and hole formation and growth in thin polymer films. Using these techniques, information has been obtained about whole chain motion both parallel and perpendicular to the plane of the film.

2.2.1   Diffusion in thin polymer films

The first measurements of in-plane chain diffusion were carried out using fluorescence recovery after patterned photobleaching (FRAPP) using fluorescently-labelled PS molecules [57]. They found that the in-plane chain diffusion in thin films was substantially slower for film thicknesses as large as 150 nm compared with that measured for very thick films. In subsequent FRAP measurements of in-plane diffusion of rubrene dye molecules in thin PS films at different temperatures, an increase in mobility was observed with decreasing film thickness, but evidence for probe segregation to the film surfaces was also obtained [58]. Although the average concentration of dye molecules in the films is low (0.6% to 3% by mass), segregation of the dye molecules to the free surface results in much larger concentrations which could artificially enhance the chain mobility by plasticizing the material in the near-surface region.

There have been considerably more studies of diffusion perpendicular to the plane of the film. Fluorescence non-radiative energy transfer (NRET) measurements of films containing layers of acceptor and donor molecules have been performed to measure diffusion perpendicular to the plane of the film, and these

measurements have revealed a decrease in the diffusion coefficient for films less than 150 nm thick [59]. Dynamic secondary ion mass spectrometry (SIMS) has been used by Rafailovich and coworkers to measure the diffusion perpendicular to the film plane on a variety of different multilayer film geometries incorporating thin layers of deuterated PS (dPS) and layers of hydrogenated PS (hPS) [60, 61], and for freely-standing PS films incorporating short dPS chains as probe molecules [62]. The dynamic SIMS measurements have revealed that the diffusion coefficient is either reduced from the bulk value over substantial distances from the substrate and the free surface [60, 61], or indistinguishable from that in bulk for freely-standing PS films incorporating probe molecules [62]. Neutron reflectometry was used to measure diffusion perpendicular to the film plane for the interface in dPS/hPS bilayer films [63], and it was found that the diffusion coefficient in thin films was unchanged from that in bulk, except for a slight decrease in the diffusion coefficient with the interface placed near the substrate. Kawaguchi *et al.* have recently used dynamic SIMS and neutron reflectometry to study the interdiffusion of the interface in hPS/dPS bilayer films [64]. They observed interface broadening at temperatures below T_g^{bulk}, indicating that there was some enhancement of mobility at the interface compared with the bulk. Boiko and Prud'homme have used lap-shear strength measurements on PS/PS interfaces which indicate that there is some interdiffusion at temperatures below T_g^{bulk} [65].

How can we reconcile the measurements of diffusion coefficients in thin polymer films, which in general show either a decrease or no change with respect to the bulk, with the observation of reduced T_g, which implies enhanced segmental mobility, in similar films? What about comparisons between the diffusion coefficient results for thin polymer films and those obtained from computer simulations of confined polymer molecules, which show increased diffusion parallel to the film plane and decreased diffusion perpendicular to the film plane, as described in detail below? To make meaningful comparisons, it is important to measure the temperature dependence of the mobility at different length scales. In particular, it is important to ask whether or not time-temperature superposition holds for the two types of motion, i.e. can the temperature dependence of the mobility at the different length scales be described by Eq. 2 using the same values of T_A and T_0, as it does (to a reasonable approximation) in bulk. Comparisons made at a single temperature could give differences that are due to a thickness dependence of the prefactor A in Eq. 2 instead of a difference in the temperature-dependent factor [15]. To properly compare the mobility at different length scales, it is important to measure the temperature dependence and to compare the values of T_0. Despite the importance of measuring the temperature dependence of the diffusion in thin polymer films, only very few studies to date have provided this information. Clearly, more effort in this area is required to make a proper evaluation of the dynamics at different length scales.

2.2.2 Dewetting and hole growth

Whole chain motion in thin polymer films can also be probed by exploiting instabilities that are inherent to thin films. Thin polymer films can be susceptible to the formation of holes when heated to temperatures that are comparable to or greater than the bulk glass transition temperature T_g^{bulk}. Obviously, if holes form and grow in the films, entire polymer molecules must move. This motion occurs initially perpendicular to the film plane, for the hole to form across the entire film thickness, and then is predominantly in the plane of the film, as the hole grows. In the absence of external fields, the instability can be driven by the van der Waals or dispersion interaction which can be substantial for film thicknesses $h < 100$ nm [66]. For films supported on substrates, it is possible for the dispersion interaction between the two film surfaces to be attractive such that the film of uniform thickness breaks up into droplets via a process known as dewetting [67, 68], or repulsive, which enhances the stability of the films [66]. Unsupported or freely-standing polymer films are always unstable to the formation and growth of holes at elevated temperatures [69, 70, 71], since the dispersion interaction is always attractive for this film geometry which is symmetric about the midplane of the film [66]. Holes can form via two different mechanisms: they can be nucleated by external perturbations or defects, such as dust or density inhomogeneities; or they can form spontaneously due to amplification of long-wavelength fluctuations of the film surfaces by the attractive dispersion or van der Waals interaction between the two film surfaces. In the case of nucleation, holes with radii R greater than a critical value R_c grow with time, where $R_c = h/2$ [72]. In the case of spontaneous hole formation, holes can form in the film due to the interplay between the dispersion and surface tension contributions to the free energy [73].

The stresses due to the dispersion interaction and surface tension which drive hole formation and growth are large in very thin films. Therefore, the whole chain motion in hole formation and growth experiments

can be considerably more complicated than that observed in chain diffusion experiments due to the presence of large stresses and the importance of nonlinear viscoelastic effects. Recent studies of the dewetting of supported PS films using scanning probe microscopy (SPM) at temperatures close to T_g^{bulk} have suggested that hole growth may occur, not by polymer flow, but rather by yielding or plastic deformation of the polymer due to the very large stresses that are produced by the interactions that drive the hole growth [74, 75]. The importance of nonlinear viscoelastic effects in interpreting these experimental results has also been considered [76, 77, 78].

Measurements of hole formation and growth in freely-standing polymer films are particularly interesting because of the very large reductions in T_g, indicative of enhanced segmental motion, that have been observed for these films [51]. Hole formation and growth in freely-standing films was first measured using optical microscopy [69, 71], in which the growth of a single hole was tracked in time. The hole radius was observed to grow exponentially with time: $R(t) = R_0 e^{t/\tau}$, where τ is the characteristic growth time. For freely-standing PS films [71], it was found that τ decreased with decreasing film thickness h. This result was interpreted in terms of the bulk phenomenon of shear thinning [79] in which the film viscosity at the edge of the hole, $\eta = \tau\epsilon/h$, where ϵ is the surface tension, decreased with increasing shear strain rate $\dot{\gamma} = 2/\tau$, according to a power law dependence $\eta \sim |\dot{\gamma}|^{-d}$ with $d = 0.65 \pm 0.03$. We have recently developed a differential pressure experiment (DPE) to measure the growth of holes in freely-standing PS films at temperatures above and below T_g^{bulk} for thicknesses that are sufficiently small such that the measured T_g values as measured using ellipsometry are reduced from the bulk value [80]. A very small pressure difference (less than 10^{-4} atm) is applied across a freely-standing polymer film, and the position of a piston is controlled to maintain a constant pressure difference across the film. When the film is heated, holes form and grow and the piston must move in one direction to maintain the constant pressure difference. The time dependence of the piston position provides a signature for hole formation and growth and it can be analyzed to obtain the characteristic growth time τ [80]. The pressure difference applied across the film does not influence the formation or growth of the holes; it is chosen to be as small as possible while still allowing the detection of the holes.

The characteristic growth times τ measured at different temperatures using the DPE for freely-standing PS films with $M_w = 2240 \times 10^3$ and three different thicknesses are shown in Fig. 9. The T_g values of the freely-standing PS films were 97°C (bulk value), 66°C and 25°C for films with $h = 91$ nm, 68 nm and 51 nm, respectively [51]. Unfortunately, τ can only be obtained for a limited range of temperatures, since measurements of the characteristic growth time τ are limited by the rapid growth of holes at temperatures $T > T_g^{\text{bulk}}$. The small shifts in temperature between the different data sets shown in Fig. 9 can be explained in terms of the bulk phenomenon of shear thinning [71, 80]. The main result of this study is that substantial hole growth occurs only for temperatures that are comparable to T_g^{bulk}, which for very thin films can be considerably higher than the reduced T_g values. Thus, the DPE results indicate that despite considerable mobility present on a segmental length scale in these films, hole growth and corresponding whole chain motion does not occur until temperatures close to the bulk value of T_g are reached.

2.3   Mobility at Surfaces

The large reductions observed in the glass transition temperature in freely-standing and supported polymer films suggest the possibility of enhanced mobility near the free surface. Many different techniques have been developed and used to probe the mobility of polymer molecules near a free surface. These experiments usually measure the diffusion of chains near the free surface, instead of segmental mobility, as detailed below.

Many measurements have been performed of the response of the free surface to mechanical perturbation using scanning probe microscopy, a variety of techniques have provided non-contact and intermittant-contact measurements of the relaxation of a perturbed surface to infer the mobility of the polymer chains in the near-surface region, and the embedding of small particles in the free surface upon heating has been studied. In addition, positron annihilation lifetime spectroscopy (PALS) has been used as a nonperturbative probe of near-surface segmental mobility.

2.3.1   Scanning probe microscopy

Scanning probe microscopy (SPM) is a powerful tool for studying the properties of surfaces of a broad range of materials. For viscoelastic materials such as polymers, it is possible not only to measure the
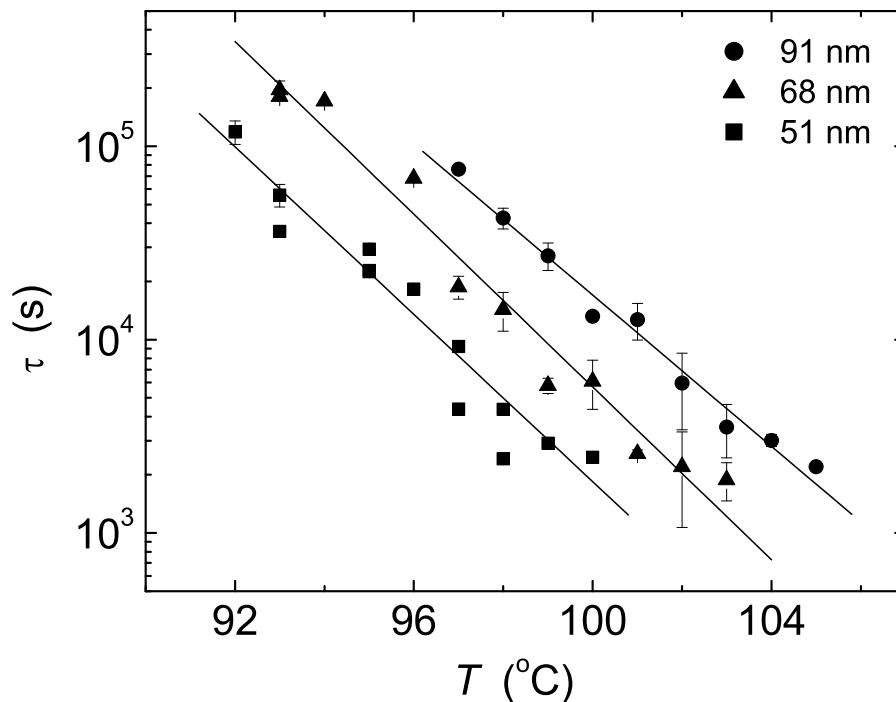
Figure 9: Characteristic growth time τ as a function of temperature T for the growth of holes in freely-standing PS films of three different thicknesses with $M_w = 2240 \times 10^3$ as measured using a differential pressure experiment [80].

surface topography but also the friction and adhesion properties by bringing the SPM tip into contact with the surface and vibrating the tip either vertically or laterally. Measurements are typically performed as a function of temperature, frequency and the load force on the SPM tip. The first studies [81, 82, 83] used lateral tip modulation, and enhanced mobility at the free surface was observed for small molecular weights which can be understood in terms of segregation of chain ends to the free surface [84]. Further measurements performed using lateral modulation of the SPM tip, also called frictional force or shear modulation force microscopy, have obtained evidence for enhanced mobility at the free surface [85, 86], as well as no change with respect to bulk properties [87]. Adhesion measurements have also been performed between polymer surfaces and SPM tips by performing force-distance curve measurements on the surface of polymer films; findings of enhanced surface mobility [88, 89] and bulk-like properties [90, 91] have been reported.

Although it is relatively easy to perform SPM measurements of a free polymer surface at elevated temperatures, the interpretation of these results is not straightforward for a number of reasons. The interaction between a rigid tip and a viscoelastic surface is very complicated [92] and obtaining an accurate estimate of the length scale over which substantial interaction between the tip and surface occurs is very difficult. The situation is further complicated because the mobility of the polymer chains is expected to vary in the near-surface region. The possibility exists of further complications due to the small contact area between the tip and surface which can result in very large stresses and could lead to nonlinear viscoelastic effects such as shear thinning [93]. It is also important to keep in mind that the results of the SPM experiments depend on the load force and scanning velocity [94]. Finally, it has been pointed out that the inference of T_g values from SPM measurements is difficult since the temperature at which a large tip response is obtained is determined by the Rouse modes and not segmental relaxation [95].

2.3.2 Relaxation of a perturbed free surface

Near-surface mobility has been measured by monitoring the smoothing of artificially roughened polymer surfaces by surface tension at elevated temperatures. These measurements have been performed using non-contact or intermittant contact methods. Tapping mode SPM has been used to monitor the decrease in surface roughness of PS surfaces that have been produced by preparing the film on a roughened CaF_2 surface [96]. The PS surfaces contained a broad range of roughnesses on different length scales, and the root-mean-square roughness measured over a sample area of 2.5×2.5 μm^2 was monitored as the samples were heated. They found that partial smoothing of nanometer-sized surface asperities occured at temperatures below bulk T_g, while full relaxation of larger features did not occur until the sample was heated to temperatures above T_g^{bulk} [96]. It has been suggested that the relaxation at smaller length scales could occur at lower temperatures because the increased curvature leads to higher Laplace pressures [75, 96], possibly even resulting in plastic deformation of the surface [75]. Measurements of the relaxation of the amplitude of sinusoidal, imprinted surface gratings (period of 600 nm, initial amplitude of 5 nm) on PS surfaces have been performed by diffracting laser light from the grating [93, 97, 98, 99]. In these measurements, evidence for surface relaxation below the bulk value of T_g was not obtained. The surface grating relaxation measurements have the advantage of probing relaxation of a well-defined wavelength, but observation of the grating amplitude decay by laser light diffraction is limited to wavelengths greater than several hundred nanometers. For smaller period gratings, tapping mode SPM could be used to monitor the decay of the amplitude, as in Ref. [96], but it is difficult to produce sinusoidal profiles with periods less than several hundred nanometers.

Rubbing of polymer surfaces with a soft cloth along one in-plane direction orients the polymer chains, and the relaxation of the oriented chains near a free surface at elevated temperatures has been used to obtain a measure of near-surface mobility. In the first study [100], near-edge x-ray absorption fine structure (NEXAFS) spectroscopy was used to monitor relaxation within the first 1 nm and the first 10 nm from the free surface, and full relaxation was not observed at temperatures below the bulk value of T_g. Recent work using optical birefringence [101, 102] and infrared-visible sum frequency generation spectroscopy (SFG) [103] has provided evidence for a surface layer with enhanced mobility that is 12 nm thick. By fitting the orientation factor as a function of temperature to a KWW (stretched exponential) function (see Eq. 1) and comparing the results for lightly rubbed and highly rubbed surfaces, they found that the activation energy was lower and the β value was larger, indicating a narrower distribution of relaxation times, for the near-surface region [103].

In another approach, NEXAFS has been used to compare the relaxation at different depths near the free surface of a 6 mm thick PS sample that was uniaxially elongated at room temperature and then heated to 60°C [104]. It was found that the orientation factor of the near-surface region of 2 nm depth decayed with a time constant that was about two-thirds that measured for the near-surface region of 200 nm depth.

It is important to keep in mind that in all of the experiments which measure the relaxation of a deformed polymer surface, the samples are intentionally prepared to be out of equilibrium so that they relax in topography or orientation when heated. To obtain meaningful comparisons between the results of these experiments and those which probe polymer mobility in flat samples that have not been purposely oriented, researchers have been careful to quantify the initial roughness or orientation and to ensure that it is not too large to avoid, e.g. nonlinear relaxation processes. In the studies involving the relaxation of artificially roughened and sinusoidal grating surfaces, care was taken to equilibrate the polymer samples at high temperature while in contact with the roughened surfaces. The roughened polymer surfaces were therefore closer to equilibrium than those measured in the experiments involving rubbed surfaces and uniaxial elongation but, even so, surface-tension-driven roughness on small length scales can lead to plastic deformation of the polymer [75].

2.3.3 Embedding of small particles in a free surface

Surface mobility has also been studied by placing small particles on a polymer surface, and measuring the extent to which the particles become embedded in the polymer surface upon heating. Obviously, the deformation of the polymer surface by the particles will depend critically on the wetting behaviour of the polymer on the particles. The penetration of small particles into the polymer surface and the adhesion of the particles to polymer surfaces has been measured using the quartz crystal microbalance (QCM) [55, 105], x-ray photoelectron spectroscopy [106] and intermittent-contact SPM measurements [107]. The size of the probing particles has been varied from nanometer-sized metal spheres and clusters to micron-sized SiC

particles. The results of experiments performed using all of these techniques indicate that embedding occurs at temperatures below that corresponding to bulk T_g. In the case of gold nanoparticles [107], it was inferred that a layer of enhanced mobility that is a few nanometers thick is present at the free surface of PS.

2.3.4 Segmental motion near a free surface

Positron annihilation lifetime spectroscopy (PALS) provides a near-surface probe, due to limited penetration depth of the positron beam, which probes local mobility. By choosing a low value of the positron energy, greater surface sensitivity is achieved, and mobility was observed to increase as the penetration depth of the positron beam was decreased [108]. T_g was found to be dramatically reduced by 57°C in the region within 5 nm of the free surface.

3 Computer simulations and theoretical models

In addition to the large body of experimental work studying chain mobility and the glass transition in thin polymer films, there has also been substantial theoretical and computer simulation work on similar systems. This work has been developed both to learn in detail about the structure and dynamics of confined glassy liquids, as well as to explain experimental data obtained for motion on different length scales.

3.1 Computer simulations of confined polymer molecules

Ideally, one would like to perform computer simulations on collections of polymer molecules that correspond to the experimental situation, i.e. long polymer chains confined to films at temperatures comparable to T_g, so that meaningful comparisons could be made. However, restrictions on computing power limit these simulations to collections of relatively short, unentangled chains with special computational techniques required either to rapidly quench the samples from high temperature or to achieve relatively low temperatures at more modest quench rates. In general, simulating the dynamics of glassy liquids is very challenging because the time scale for motion becomes extremely slow as the temperature is lowered toward the glass transition. As a result, there have been relatively few simulations of either confined glassy polymer films or supercooled polymer melts, and detailed comparisons between the results that have been obtained from computer simulations and those obtained from experiments are difficult. Nevertheless, the rich behaviour of the static and dynamic properties of confined polymer chains obtained from computational studies provides considerable insight and guidance for the experimental studies.

The computer simulations have focused on the static and dynamic properties of collections of short, unentangled polymer chains confined between walls, and the effect of changing chain length, density, wall separation, wall potential, wall roughness and temperature. Mansfield and Theodorou [109] used molecular dynamics (MD) to study the static and dynamic properties of freely-standing polypropylene films at a temperature lower than the experimental value of T_g. They achieved such low temperatures by using a special equilibration strategy based on consecutive MD runs on different ensembles of the system. They found that the center-of-mass mobility parallel to the walls was enhanced for chains located a distance of the order of R_{ee} from the free surfaces. Baschnagel and Binder [110] used Monte Carlo (MC) techniques to examine the static and dynamic properties of a supercooled polymer melt confined between hard neutral walls. Use of so-called "slithering snake dynamics" [111] allowed the equilibration of the polymer configurations in times that were orders of magnitude faster than those simulated using conventional Rouse dynamics. They found that the motion of the chain segments and the chains parallel to the wall were enhanced, and that motion perpendicular to the walls was reduced, over a length scale that was of the order of R_{ee}. Anisotropy in the dynamic properties of confined molecules has also been observed in simulations performed at higher temperatures [112, 113, 114, 115]. Recent MD simulations by Baschnagel and coworkers have focused on several features: (1) the modeling of free surfaces using a "softer" wall potential ($\sim z^{-9}$, where z is the distance from the wall) than that within the film ($\sim z^{-12}$) [116], which resulted in enhanced mean-square-displacements, i.e. accelerated dynamics, next to the walls; and (2) the decrease with wall separation of the mode coupling temperature T_c, instead of T_g, which depends on cooling rate, or the Vogel temperature T_0 (see Eq. 2), the existence of which is postulated but cannot be derived [116, 117]. The effect of the roughness of the walls on the dynamics was studied using MD for supercooled liquids confined to narrow pores [118].

Rough walls produced a large increase in relaxation times close to the wall compared with relaxation times obtained for smooth walls. A hard sphere MD technique has been used to simulate both supported and freely-standing polymer films [119]. An apparent glass transition temperature was identified after a stepped cooling sequence by monitoring the film thickness as a function of temperature and also by extrapolating the temperature dependence of mobility to low temperatures. Slower dynamics in the chains next to the walls and increased T_g values were observed for strongly attractive walls, whereas enhanced dynamics and substantially decreased T_g values were observed for weakly attractive walls and freely-standing films.

3.2 Theories for enhanced mobility in thin films

A substantial number of theoretical models have been proposed to explain the observed changes to T_g in thin polymer films. Comparisons between freely-standing and supported film T_g results suggest that chain segments near a free surface have a higher mobility than in the bulk. As a result, the models focus on the enhanced mobility at the free surface and mechanisms by which this increased mobility can be propagated deeper into the film. In terms of explaining the large body of experimental results that has been obtained for supported and freely-standing films, no one theoretical model is successful in explaining all of the data. Most of the models have been developed specifically to explain the results obtained for supported polymer films and low M_w freely-standing films, for which the T_g reductions are independent of M_w.

A simple scaling argument was proposed to suggest that the T_g value near the free surface will be lower than the bulk value due to segregation of the chain ends to the free surface of the film [84]. This model provides good agreement with experimental results obtained for very low M_w supported films for which the density of chain ends is substantial [120].

In interpreting the experimental results, various groups have assumed a variation in mobility across the thickness of the film and have modeled this using a layer model in which there is assumed to be a more mobile layer near the free surface, and a less mobile layer near the polymer-substrate interface (for supported films). If one assumes that the layer thicknesses are independent of temperature, this leads to a dependence of the difference between the T_g value for the film and the bulk T_g value on the overall film thickness h given by $[T_g(h) - T_g^{\text{bulk}}] \sim 1/h$. This dependence is certainly not observed experimentally for freely-standing films, and for supported films, for which the T_g reductions are much smaller than for freely-standing films, this dependence has not been shown convincingly. Forrest and Mattsson have shown that allowing the mobile layer at the free surface to have a thickness which increases with decreasing temperature, in the same manner as the length scale for cooperative motion, one obtains excellent agreement between the measured T_g values and the average values calculated using the layer model for both low M_w freely-standing films and supported films [42].

A model has been proposed that considers the glass transition in thin polymer films obtained upon cooling as the freezing of the polymer due to memory effects in the viscoelastic modes of the film, using concepts from mode coupling theory [121, 122]. Quantitative agreement is achieved with $T_g(h)$ reductions in low molecular weight PS films with only one adjustable parameter, the Young's modulus of the film at T_g.

Ngai has applied the "coupling model" [123, 124, 125] to the case of thin polymer films [95, 126]. For thin polymer films, it is suggested that the presence of the surface results in orientation of the chain segments parallel to the surface with a corresponding reduction in the number of contacts between segments (intermolecular coupling). The reduction in intermolecular coupling leads to reductions in T_g which are in qualitative agreement with experimental results obtained for supported and freely-standing films.

A model based on the concept of percolation incorporating spatial heterogeneity has been proposed in which the film is subdivided into regions with "fast" and "slow" mobility [127, 128]. T_g is defined as a three-dimensional percolation of "slow" domains, and reduced values of T_g are obtained for thin films since percolation need only occur over a limited number of layers of the domains (quasi-two-dimensional percolation). This model gives agreement with T_g data obtained for supported polymer films.

One proposed model attributes the $T_g(h)$ reductions observed for thin polymer films to an inhomogeneous density profile, with the $T_g(h)$ value of the inhomogeneous film corresponding to that of a bulk homogeneous sample with the same average density [129]. However, it has been shown that the average density of thin PS films is the same as the bulk density of PS to within 0.5% for freely-standing PS films which have T_g reductions of up to 25% [49], and 1% for supported PS films [130].

One model has been developed specifically to explain the unique M_w-dependent $T_g(h)$ behaviour observed

for high M_w freely-standing films. Based on free volume arguments, de Gennes has proposed a new mode of mobility ("sliding mode") to explain $T_g(h)$ reductions in high M_w freely-standing films [40]. As the film thickness is decreased, more chain segments in a given chain contact the free surfaces. The segments in contact with one of the free surfaces are assumed to be more mobile because they have fewer constraints than those segments inside the film. Because of the chain connectivity, the new mode allows for sliding of chain segments that link free surface segments on the same film surface ("loops") and on different film surfaces ("bridges"). Therefore, this model provides a mechanism by which the enhanced mobility of the segments in contact with the free surfaces can give rise to mobility over distances that are comparable to the overall size of the polymer molecule, and qualitative agreement is obtained with the experimental results for high M_w freely-standing PS films. We point out that because the large T_g reductions observed for freely-standing PS films reveal well-defined, reproducible dependences of T_g on h and M_w [51, 54], this data set provides a good starting point for critical tests of de Gennes' theory, as well as new theories, of chain confinement effects in the T_g behaviour of thin polymer films.

There has also been a very interesting analytical calculation by Semenov for very thin films of long, entangled molecules in which he finds that diffusion of chains is dramatically suppressed due to excluded volume effects which prevent the relaxation of local changes in density due to reptation while segmental mobility is not affected [131]. This mechanism demonstrates that motion on different length scales can be very different indeed.

In this section, we have described many different models that have been developed to interpret the $T_g(h)$ behaviour observed experimentally in thin polymer films. Each approach has its successes, but there seems to be no clear reason to choose one approach over another. This situation indicates two difficulties associated with the study of the glass transition in thin polymer films. First of all, the glass transition in bulk samples is not yet well-understood, so the identification of the physical mechanism or mechanisms that are important in confined systems is not clear. Secondly, the quality and scope of the glass transition data obtained for thin polymer films is not sufficient to allow the preference of one model over the others. Clearly, much additional work, both experimental and theoretical, is required to resolve this issue.

4   Important Issues and Questions

The experimental, theoretical and computational studies of thin polymer films that have been performed to date have resulted in considerable understanding of the effect of confinement on polymer mobility, but they have also led to a number of important issues and questions. Some of these issues are directly related to the intriguing results obtained for freely-standing films, as discussed above: (1) the existence of the common intersection point on the plot of T_g versus h for films with different, large M_w values (see Fig. 6); (2) the crossover between a M_w-dependence for high M_w films, indicative of chain confinement effects, and the lack of M_w-dependence for low M_w films; (3) the sharpness of the glass transition observed with both BLS and ellipsometry for freely-standing PS films. All of these features of the freely-standing film data deserve more study. In addition, there are more general issues and questions related to mobility in very thin polymer films that impact many of the studies discussed above.

4.1   Mobility on different length scales

Much experimental evidence for the reduction of T_g with decreasing film thickness has been obtained from a variety of studies. In contrast, studies that have focused on measurements of the movement of entire polymer chains have found no measurable enhancement of the chain mobility, and even a decrease in the chain mobility, in very thin polymer films. This difference in the mobility on different length scales is most dramatic in the case of freely-standing films for which very thin films show reductions in T_g of tens of degrees but no substantial hole formation is observed upon heating until temperatures comparable to the bulk value of T_g are reached [80]. We can suggest several ways in which this apparent contradiction between the results of these two measurements can be resolved. Since the formation of a hole requires the motion of chains across the entire thickness of the film, the dramatic difference between T_g and the temperature at which substantial hole formation and growth occurs upon heating of the films may indicate a variation in mobility across the thickness of the film, with the more mobile segments near the free surface. This is certainly consistent with the existence of a more mobile layer at the free surface of the film inferred

from other experiments. The apparent contradiction could also be explained by large differences in the polymer mobility parallel and perpendicular to the film. Formation of a hole requires motion of entire chains perpendicular to the plane of the film, whereas segmental motion could be enhanced parallel to the plane of the film. This anisotropy in mobility is qualitatively consistent with that observed in computer simulations. The apparent contradiction between the T_g and hole formation data for freely-standing PS films could also be an indication of the decoupling of segmental and chain motion in very thin polymer films, as for the mechanism proposed by Semenov [131]. The decoupling of segmental and chain motions in thin polymer films has implications for time-temperature superposition according to Eq. 2, which is found to hold rather well in bulk. However, in thin films, the temperature dependence of the two types of motion might not be the same. This might occur because motions greater than some length scale comparable to the overall size of the molecule are suppressed at temperatures comparable to T_g in very thin polymer films, which is consistent with the experimentally-observed decrease in contrast of the thermal expansion of the glass and melt with decreasing film thickness [105]. The current situation is that there are several possible explanations, but no definitive resolution, for this issue, and it highlights the importance of understanding the nature of the mobility being probed in a given experiment so that meaningful comparisons of different experimental studies can be made.

4.2   Length scale for changes in mobility

A key result in the measurement of T_g in thin polymer films is the observation of changes in the average T_g value with film thickness for film thicknesses that are large compared with the size of the cooperatively rearranging region which is only several nanometers in size [7, 8]. Most theoretical models that have been developed to interpret experimental results have focused on enhanced mobility near the free surface of a thin polymer film. In addition to models which postulate mechanisms for enhanced mobility over length scales much larger than the change in density near the free surface, considerable success in fitting experimental measurements of the average mobility has been obtained using layer models in which the variation in mobility with distance from the film interfaces is modelled as homogeneous layers of different mobility. Using layer models, estimates of the spatial extent of the enhanced mobility due to the free surface have been obtained from comparisons between average T_g values measured for PS films of different thickness from PALS measurements [42], heat capacity jumps observed for PS spheres [21], as well as the T_g values inferred for a free surface [108], the relaxation of perturbed surfaces [101, 102, 103, 104] and the embedding of small particles [107]. These estimates range from several nanometers to approximately 10 nm. Computer simulations on confined polymer systems, which have the advantage of allowing the determination of detailed information concerning the distance- and direction-dependent mobility with respect to a confining wall, have revealed changes to the dynamics over distances from the confining walls that are comparable to R_{ee} [109, 110, 116, 119], which is of the order of several nanometers for the short molecules used in the simulations.

It is expected that the dynamical behaviour will vary smoothly with distance from the free surface. The layer models approximate this smooth variation in a rather crude manner: it is modelled as an abrupt transition from an outer layer of uniformly fast dynamics to an inner layer of uniformly bulk dynamics. Ideally, one would like to have the ability to probe the mobility as a function of distance from the film interfaces, as suggested in Refs. [40, 41]. This has been provided by the recent depth-dependent T_g measurements of Ellison and Torkelson [35]. This detailed study has shown convincingly that there are reductions in T_g near a free surface that extend over distances of tens of nanometers from the free surface. This length scale for enhanced mobility near a free surface is considerably larger than that inferred from layer model interpretations of previous data, and this suggests that the use of layer models may be inadequate to interpret measurements which probe the average mobility of the film. The study of Ellison and Torkelson has also addressed the effect of confinement on the distribution of T_g values with distance from the free surface. In principle, it is possible that T_g reductions near a free surface may be due to the influence of the free surface, due to confinement within a thin film, or due to both effects. Ellison and Torkelson have demonstrated clearly that both free surface and confinement effects are important: there are reductions in T_g near a free surface that extend over distances of tens of nanometers from the free surface, but the magnitude of the reduction at the free surface can also depend on the overall thickness of the film. If the film is sufficiently thin, compared with the spatial extent of T_g reductions from the free surface, the reduction in T_g at the free surface is less

than that observed for the free surface of a very thick film, even though the average T_g value for the thin film is less than that of the thick film. The approach of using fluorescently-tagged layers within multilayer films holds much promise to more completely elucidate the detailed T_g behaviour near free polymer surfaces and within thin polymer films.

4.3 Non-equilibrium nature of thin polymer films

Spincoating of dilute polymer solutions onto substrates is a powerful technique that allows the deposition of thin polymer films of uniform thickness ranging from nanometers to micrometers. However, the glassy polymer film produced by rapid evaporation of the solvent (solvent quench) differs from that produced by a temperature quench in that there are unwanted solvent molecules present during the solvent quench as well as orientation of the polymer chains along the radial direction. As the solvent content is reduced during spincoating, during a time determined by the volatility of the solvent, the glassy state "freezes in" below a critical concentration, which for polystyrene in toluene at 25°C is 14% by mass of toluene [132]. This means that the material undergoes a large shrinkage in the glassy state as the remaining solvent molecules are removed. In addition, since evaporation takes place at the free surface of the film, flow instabilities and the formation of a "crust" can be obtained [133, 134, 135]. Annealing of the films at temperatures greater than the bulk value of T_g is typically performed after spincoating to allow the chains to relax, but stress relaxation can be inhibited by attractive interactions between the polymer molecules and the substrate. In addition, there is a tendency for the film to break up or dewet at elevated temperatures due to nucleation of holes at defects, e.g. dust or density inhomogeneities, or by amplification of thermal fluctuations of the free surface of the film for the cases in which the dispersion interaction acting across the film is attractive. Therefore the annealing process is a tradeoff between relaxing the chains and preventing the dewetting of the film, and the best criteria for producing a glassy polymer film is not unambiguously defined.

Ideally, the spincoated polymer films would be heated to a sufficiently high temperature for a sufficiently long time to allow the molecules to diffuse by a distance which is at least comparable to the overall size of the molecule. This time, also called the reptation time $\tau_r \sim M_w^{3.4}$, can be identified as the time corresponding to the transition between the plateau and terminal flow regions on the $J(t)$ curve shown in Figure 4. For the annealing of PS films at $T = 115$°C for 12 h (typical conditions) [51], the annealing time is less than τ_r for $M_w > 850 \times 10^3$. It has been argued that, for the purposes of T_g measurements, it is only necessary to anneal the films for times that are sufficient to allow chain segments between entanglement points to relax, and these times are substantially less than τ_r for high M_w polymers [51]. One has to also consider the effect on T_g of changes to the chain conformation and entanglement produced by sample preparation, e.g. radial stretching of the molecules due to the spincoating process. If the T_g reductions were due to the distortion of the chain conformations, then this would be observed for all film thicknesses and the distinctive $T_g(h)$ behaviour in Figure 6, with bulk T_g values for large film thickness and reduced T_g values below a threshold film thickness value, would not be observed. Recent experimental studies have found that reductions in the entanglement density in spincoated polymer films are not responsible for T_g reductions in thin polymer films [30, 136].

5 Summary

It has been twelve years since Jackson and McKenna [13] reported reductions in T_g for organic liquids confined to porous glasses, ten years since Reiter [56] found evidence for enhanced mobility in dewetting studies of thin polymer films, and nine years since Keddie *et al.* [23] presented the first systematic study of T_g reductions in thin polymer films with decreasing film thickness. Since then, extensive experimental, theoretical and computational efforts have focused on trying to explain these original, provocative results. By focusing on well-defined experimental confining geometries such as supported single and multilayer polymer films and freely-standing polymer films, with corresponding theories and computer simulations for these geometries, much has been learned of the effect of the film interfaces and free surfaces on the glass transition and chain diffusion. These studies have also provided additional surprising results. In particular, the results obtained for freely-standing polymer films are unique and remarkable, and further developments of experiments and theories are needed to understand this behaviour in detail. In addition, considerable experimental evidence has been obtained that shows that segmental mobility can be enhanced in very thin polymer films while

chain diffusion is unchanged from that in bulk. This behaviour is another indication that dynamics in thin polymer films can be considerably different from that in bulk. The development of new experimental techniques to study the dynamics of polymers at free surfaces provides the promise of new insights, but additional effort is required to develop the proper analysis of the data, especially those involving mechanical deformation of polymers at elevated temperatures, so that the results obtained using different techniques can be meaningfully compared. The use of new and improved experimental techniques and sophisticated sample geometries, combined with advances in theoretical analyses and computer simulations, will ensure that the study of dynamics in thin polymer films remains a rich area of research, leading to a deeper understanding of mobility of confined polymer molecules on different length scales.

Acknowledgments

References

[1] S Brawer. Relaxation in Viscous Liquids and Glasses. Columbus: The American Ceramic Society, 1985.

[2] MD Ediger. Annu Rev Phys Chem 51: 99, 2000.

[3] E Donth. The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials. Berlin: Springer Verlag, 2001.

[4] CA Angell, KL Ngai, GB McKenna, PF McMillan, SW Martin. J Appl Phys 88: 3113, 2000.

[5] MH Cohen, D Turnbull. J Chem Phys 31: 1164, 1959.

[6] G Adam, JH Gibbs. J Chem Phys 43: 139, 1965.

[7] E Hempel, G Hempel, A Hensel, C Schick, E Donth. J Phys Chem B 104: 2460, 2000.

[8] SA Reinsberg, XH Qui, M Wilhelm, HW Spiess, MD Ediger. J Chem Phys 114: 7299, 2001.

[9] C Donati, JF Douglas, W Kob, SJ Plimpton, PH Poole, SC Glotzer. Phys Rev Lett 80: 2338, 1998.

[10] G Strobl. The Physics of Polymers, Second Edition. Berlin: Springer Verlag, 1997.

[11] DJ Plazek, XD Zheng, KL Ngai. Macromolecules 25: 4920, 1992.

[12] KL Ngai, DJ Plazek. Rubber Chem Technol 68: 376, 1995.

[13] CL Jackson, GB McKenna. J Non-Cryst Solids 131-133: 221, 1991.

[14] Proceedings of the International Workshop on Dynamics in Confinement. J Phys IV 10: Pr7-3 - Pr7-346, 2000.

[15] JA Forrest, RAL Jones. In: A Karim, S Kumar, ed. Polymer Surfaces, Interfaces and Thin Films. Singapore: World Scientific, 2000.

[16] JA Forrest, K Dalnoki-Veress. Adv Colloid Interface Sci 94: 167, 2001.

[17] Special issue on Properties of Thin Polymer Films. Eur Phys J E 8: 101-266, 2002.

[18] M Schick, E Donth. Phys Scr 43: 423, 1991.

[19] J-Y Park, GB McKenna. Phys Rev B 61: 6667, 2000.

[20] SH Anastasiadis, K Karatasos, G Vlachos, E Manias, EP Gianellis. Phys Rev Lett 84: 915, 2000.

[21] T Sasaki, A Shimizu, TH Mourey, CT Thurau, MD Ediger. J Chem Phys 119: 8730, 2003.

[22] B Frick, K Dalnoki-Veress, JA Forrest, JR Dutcher, CA Muray, A Higgins. Eur Phys J E, in press.

[23] JL Keddie, RAL Jones, RA Cory. Europhys Lett 27: 59, 1994.

[24] JA Forrest, K Dalnoki-Veress, JR Dutcher. Phys Rev E 56: 5705, 1997.

[25] JL Keddie, RAL Jones. Israel J Chem 35: 21, 1995.

[26] OKC Tsui, HF Zhang. Macromolecules 34: 9139, 2001.

[27] S Kawana, RAL Jones. Phys Rev E 63: 021501, 2001.

[28] K Fukao, Y Miyamoto. Phys Rev E 61: 1743, 2000.

[29] K Fukao, Y Miyamoto. Europhys Lett 46: 649, 1999.

[30] OKC Tsui, TP Russell, CJ Hawker. Macromolecules 34: 5535, 2001.

[31] GB DeMaggio, WE Frieze, DW Gidley, M Zhu, HA Hristov, AF Yee. Phys Rev Lett 78: 1524, 1997.

[32] DS Fryer, PF Nealey, JJ de Pablo. Macromolecules 33: 6439, 2000.

[33] CJ Ellison, JM Torkelson. J Polym Sci, Part B: Polm Phys 40: 2745, 2002.

[34] CJ Ellison, SD Kim, DB Hall, JM Torkelson. Eur Phys J E 8: 155, 2002.

[35] CJ Ellison, JM Torkelson. Nature Mater 2: 695, 2003.

[36] JL Keddie, RAL Jones, RA Cory. Faraday Discuss 98: 219, 1994.

[37] JH van Zanten, WE Wallace, W-L Wu. Phys Rev E 53: R2053, 1996.

[38] L Hartmann, W Gorbatschow, J Hauwecte, F Kremer. Eur Phys J E 8: 145, 2002.

[39] JS Sharp, JA Forrest. Phys Rev E 67: 031805, 2003.

[40] P-G de Gennes. Eur Phys J E 2: 201, 2000.

[41] RAL Jones. Eur Phys J E 2: 205, 2000.

[42] JA Forrest, J Mattsson. Phys Rev E 61: R53, 2000.

[43] DB Hall, JC Hooker, JM Torkelson. Macromolecules 30: 667, 1997.

[44] K Fukao, S Uno, Y Miyamoto, A Hoshino, H Miyaji. Phys Rev E 64: 051807, 2001.

[45] M Wübbenhorst, CA Murray, JA Forrest, JR Dutcher. Proceedings of the 11th Symposium on Electrets, Melbourne, 2002. New York: IEEE, in press.

[46] M Wübbenhorst, CA Murray, JR Dutcher. Eur Phys J E, in press.

[47] J van Turnhout, M Wübbenhorst. J Non-Cryst Solids 305: 50, 2002.

[48] JA Forrest, K Dalnoki-Veress, JR Stevens, JR Dutcher. Phys Rev Lett 77: 2002, 1996; Phys Rev Lett 77: 4108, 1996.

[49] JA Forrest, K Dalnoki-Veress, JR Dutcher. Phys Rev E 58: 6109, 1998.

[50] J Mattsson, JA Forrest, L Börjesson. Phys Rev E 62: 5187, 2000.

[51] K Dalnoki-Veress, JA Forrest, C Murray, C Gigault, JR Dutcher. Phys Rev E 63: 031801, 2001.

[52] CB Roth, JR Dutcher. Eur Phys J E, in press.

[53] JR Dutcher, K Dalnoki-Veress, JA Forrest. In: G Warr, S Manne, ed. Supramolecular Structure in Confined Geometries. American Chemical Society Symposium Series 736: 127-139, 1999.

[54] K Dalnoki-Veress, JA Forrest, PG de Gennes and JR Dutcher. J Phys IV 10: Pr7-221, 2000.

[55] JA Forrest, C Svanberg, K Révész, M Rodahl, LM Torell, B Kasemo. Phys Rev E 58: R1226, 1998.

[56] G Reiter. Europhys Lett 23: 579, 1993.

[57] B Frank, AP Gast, TP Russell, HR Brown, C Hawker. Macromolecules 29: 6531, 1996.

[58] KC Tseng, NJ Turro, CJ Durning. Phys Rev E 61: 1800, 2000.

[59] DB Hall, JM Torkelson. Macromolecules 31: 8817, 1998.

[60] X Zheng, MH Rafailovich, J Sokolov, Y Strzhemechny, SA Schwarz, BB Sauer, M Rubinstein. Phys Rev Lett 79: 241, 1997.

[61] Y Pu, MH Rafailovich, J Sokolov, D Gersappe, T Peterson, W-L Wu, SA Schwarz. Phys Rev Lett 87: 206101, 2001.

[62] Y Pu, H White, MH Rafailovich, J Sokolov, A Patel, C White, W-L Wu, V Zaitsev, SA Schwarz. Macromolecules 34: 8518, 2001.

[63] T Kuhlmann, J Kraus, P Müller-Buschbaum, DW Schubert, M Stamm. J Non-Cryst Solids 235-237: 457, 1998.

[64] D Kawaguchi, K Tanaka, T Kajiyama, A Takahara, S Tasaki. Macromolecules 36: 1235, 2003.

[65] YM Boiko, RE Prud'homme. J Polym Sci, Part B: Polm Phys 36: 567, 1998.

[66] JN Israelachvili. Intermolecular & Surface Forces, Second edition. San Diego, Academic, 1991.

[67] G Reiter. Phys Rev Lett 68: 75, 1992.

[68] F Brochard-Wyart, J Daillant. Can J Phys 68: 1084, 1990.

[69] G Debrégeas, P Martin, F Brochard-Wyart. Phys Rev Lett 75: 3886, 1995.

[70] G Debrégeas, P-G de Gennes, F Brochard-Wyart. Science 279: 1704, 1998.

[71] K Dalnoki-Veress, BG Nickel, C Roth, JR Dutcher. Phys Rev E 59: 2153, 1999.

[72] JD Gunton, M San Miguel, PS Sahni. In: C Domb, JL Lebowitz, ed. Phase Transitions and Critical Phenomena, Vol 8. London: Academic Press, 1983.

[73] A Vrij, F Th Hesselink, J Lucassen, M Van Den Tempel. Koninkl Nederl Academie van Wetenschappen Amsterdam B 73: 124 1970.

[74] G Reiter. Phys Rev Lett 87: 186101, 2001.

[75] G Reiter. Eur Phys J E 8: 251, 2002.

[76] F Saulnier, E Raphaël, P-G de Gennes. Phys Rev Lett 88: 196101, 2002.

[77] F Saulnier, E Raphaël, P-G de Gennes. Phys Rev E 66: 061607, 2002.

[78] V Shenoy, A Sharma. Phys Rev Lett 88: 236101, 2002.

[79] WW Graessley. Adv Polym Sci 16: 1, 1974.

[80] CB Roth, BG Nickel, JR Dutcher, K Dalnoki-Veress. Rev Sci Instrum 74: 2796, 2003.

[81] T Kajiyama, K Tanaka, N Satomi, A Takahara. Macromolecules 31: 5150, 1998.

[82] N Satomi, A Takahara, T Kajiyama. Macromolecules 32: 4474, 1999.

[83] K Tanaka, A Takahara, T Kajiyama. Macromolecules 33: 7588, 2000.

[84] AM Mayes. Macromolecules 27: 3114, 1994.

[85] JA Hammerschmidt, WL Gladfelter, G Haugstad. Macromolecules 32: 3360, 1999.

[86] H Fischer. Macromolecules 35: 3592, 2002.

[87] S Ge, Y Pu, W Zhang, M Rafailovich, J Sokolov, C Buenviaje, R Buckmaster, RM Overney. Phys Rev Lett 85: 2340, 2000.

[88] H van Melick, A van Dijken, J den Toonder, L Govaert, H Meijer. Phil Mag A 82: 2093, 2002.

[89] VN Bliznyuk, HE Assender, GAD Briggs. Macromolecules 35: 6613, 2002.

[90] OKC Tsui, XP Wang, JYL Ho, TK Ng, X Xiao. Macromolecules 33: 4198, 2000.

[91] XP Wang, XD Xiao, OKC Tsui. Macromolecules 34: 4180, 2001.

[92] TCT Ting. J Appl Mech 33: 845, 1966.

[93] D Johannsmann. Eur Phys J E 8: 257, 2002.

[94] F Dinelli, C Buenviaje, RM Overney. J Chem Phys 113: 2043, 2000.

[95] K Ngai. Eur Phys J E 8: 225, 2002.

[96] T Kerle, Z Lin, H-C Kim, TP Russell. Macromolecules 34: 3484, 2001.

[97] M Hamdorf, D Johannsmann. J Chem Phys 112: 4262, 2000.

[98] M Hamdorf, D Johannsmann. J Chem Phys 114: 9685, 2001.

[99] K Petersen, D Johannsmann. J Non-Cryst Solids 307-310: 532, 2002.

[100] Y Liu, TP Russell, MG Samant, J Stöhr, HR Brown, A Cossy-Favre, J Diaz. Macromolecules 30: 7768, 1997.

[101] AD Schwab, DMG Agra, JH Kim, S Kumar, A Dhinojwala. Macromolecules 33: 4903, 2000.

[102] DMG Agra, AD Schwab, JH Kim, S Kumar, A Dhinojwala. Europhys Lett 51: 655, 2000.

[103] AD Schwab, A Dhinojwala. Phys Rev E 67: 021802, 2003.

[104] WE Wallace, DA Fischer, K Efimenko, W-L Wu, J Genzer. Macromolecules 34: 5081, 2001.

[105] JA Forrest, J Mattsson, L Börjesson. Eur Phys J E 8: 129, 2002.

[106] V Zaporojtchenko, T Strunskus, J Erichsen, F Faupel. Macromolecules 34: 1125, 2001.

[107] JH Teichroeb, JA Forrest. Phys Rev Lett 91: 016104, 2003.

[108] YC Jean, R Zhang, H Cao, J-P Yuan, C-M Huang, B Nielsen, P Asoka-Kumar. Phys Rev B 56: R8459, 1997.

[109] KF Mansfield, DN Theodorou. Macromolecules 24: 6283, 1991.

[110] J Baschnagel, K Binder. J Phys I France 6: 1271, 1996.

[111] K Kremer, K Binder. Comput Phys Rep 7: 259, 1988.

[112] KF Mansfield, DN Theodorou. Macromolecules 22: 3143, 1989.

[113] I Bitsanis, G Hadziioannau. J Chem Phys 92: 3827, 1990.

[114] T Matsuda, GD Smith, RG Winkler, DY Yoon. Macromolecules 28: 165, 1995.

[115] P Doruker, W L Mattice. Macromolecules 32: 194, 1999.

[116] F Varnik, J Baschnagel, K Binder. Phys Rev E 65: 021507, 2002.

[117] F Varnik, J Baschnagel, K Binder. Eur Phys J E 8: 175, 2002.

[118] P Scheidler, W Kob, K Binder. Europhys Lett 59: 701, 2002.

[119] JA Torres, PF Nealey, JJ de Pablo. Phys Rev Lett 85: 3221, 2000.

[120] K Tanaka, A Taura, S-R Ge, A Takahara, T Kajiyama. Macromolecules 29: 3040, 1996.

[121] S Herminghaus, K Jacobs, R Seemann. Eur Phys J E 5: 531, 2001.

[122] S Herminghaus. Eur Phys J E 8: 237, 2002.

[123] KL Ngai. Commun Solid State Phys 9: 121, 1979.

[124] K-Y Tsang, KL Ngai. Phys Rev E 54: R3067, 1996.

[125] K-Y Tsang, KL Ngai. Phys Rev E 56: R17, 1997.

[126] K Ngai, Rizos. Mater Res Soc Proc 455: 147, 1997.

[127] D Long, F Lequeux. Eur Phys J E 4: 371, 2001.

[128] S Merabia, D Long. Eur Phys J E 9: 195, 2002.

[129] JD McCoy, JG Curro. J Chem Phys 116: 9154, 2002.

[130] WE Wallace, NC Beck Tan, WL Wu, S Satija. J Chem Phys 108: 3798 (1998).

[131] AN Semenov. Phys Rev Lett 80: 1908, 1998.

[132] GB McKenna. J Phys IV 10: Pr7-53, 2000.

[133] KE Strawhecker, SK Kumar, JF Douglas, A Karim. Macromolecules 34: 4669, 2001.

[134] P-G de Gennes. Eur Phys J E 6: 421, 2001.

[135] P-G de Gennes. Eur Phys J E 7: 31, 2002.

[136] P Bernazzani, SL Simon, DJ Plazek, KL Ngai. Eur Phys J E 8: 201, 2002.