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Glass transition and chain mobility in thin polymer films

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Abstract

We review recent work on the motion of polymer molecules confined to thin films. There has been considerable experimental evidence for large reductions in the glass transition temperature T_g with decreasing film thickness, indicative of enhanced segmental motion, while the motion of entire molecules is essentially unchanged from that in bulk samples. General trends in the data are highlighted and outstanding issues are discussed.

Keywords: Polymer thin films; Glass transition; Chain mobility

1. Introduction

Thin polymer films with thicknesses of tens of nanometers are studied extensively 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.

A polymer molecule can be described on a variety of different length scales, ranging from the size of the individual monomers to the overall size of the molecule R_{ee}. The characteristic time scales range from that corresponding to segmental relaxation, related to the glass transition, to that corresponding to the motion of entire chains. 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. For example, the effect of confinement on the segmental motion of polymers has been studied using a variety of experimental geometries: interfaces in semicrystalline polymers [1], polymer solutions in porous glasses [2], polymers intercalated into the 2 nm gaps of layered compounds [3], polymer spheres with diameters of tens of nanometers [4], and thin polymer films.

The thin film sample geometry is appealing since it is straightforward to control the interactions at the free surface and film|substrate interface, 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 the effect of one-dimensional confinement on the dynamics of polymer molecules on a variety of length scales comparable to those of the polymer molecules. To probe the molecular mobility in thin polymer films, it is necessary to use techniques that have 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 whole chain motion 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

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[5], but the requirements for sample preparation are very demanding. Instead, new techniques have been developed and existing techniques have been adapted to obtain measures of the molecular mobility on different length scales in thin polymer films.

In Section 2, we describe the results of recent experimental studies of the glass transition in thin polymer films. 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 [6–9]). In contrast, it is found that whole chain motion in thin polymer films is not substantially different from that in bulk, as discussed in Section 3. A discussion and summary of the results are given in Section 4.

2. Glass transition in thin polymer films

In the simplest picture, the glass transition describes the change from a rubber-like liquid to a glassy or amorphous solid as a material is cooled. A detailed understanding of the glass transition in bulk samples has remained elusive; for a discussion of the relevant issues, see [10,11]. However, the concepts of free volume [12] and cooperative motion [13] have been useful in trying to explain the dramatic reduction in molecular mobility with decreasing temperature. 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 [12]. One way to achieve motion at low 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 [13] postulated the existence of cooperatively rearranging regions or CRRs as the smallest regions at a given temperature that can rearrange independent of neighbouring regions, with the size of the CRR increasing with decreasing temperature. Experiments indicate that the size of these regions is several nanometers [14,15]. The possible existence of the cooperativity length scale of Adam and Gibbs 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. Finite size effects on T_g were first observed by Jackson and McKenna [16] for simple liquids confined within porous glasses with pore diameters on the nanometer scale. This original work has led to extensive experimental and theoretical studies of the effect of confinement on the glass transition using a variety of different sample geometries and different molecules (see, for example [17,18]). We will focus on experimental results obtained for polymer molecules confined to supported and freely standing thin films.

2.1. 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. [19] using ellipsometry. 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 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 nm < h < 200 nm and molar masses $120 \times 10^3 < M_w < 2900 \times 10^3$. They measured reductions in T_g for h < 40 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:

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

where α = 3.2 nm and δ = 1.8. A compilation of results obtained for PS films on a variety of substrates using numerous experimental techniques such as ellipsometry [19–23], dielectric spectroscopy [24,25], X-ray reflectivity [26], positron annihilation lifetime spectroscopy (PALS) [27], local thermal analysis [28] and probe fluorescence intensity [29–31] is shown in Fig. 1. The trend in the data

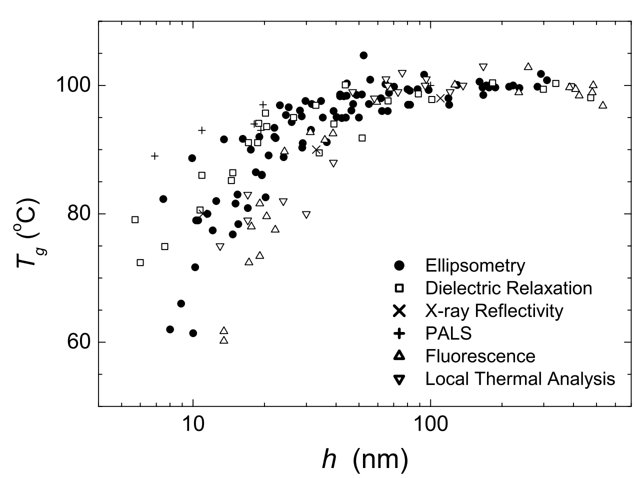

Fig. 1. Glass transition temperature T_g as a function of film thickness h measured for polystyrene (PS) films of different molar masses M_w supported on a variety of substrates using six different techniques: ellipsometry [19–23], dielectric relaxation [25], X-ray reflectivity [26], positron annihilation lifetime spectroscopy (PALS) [27], fluorescence intensity [31], and local thermal analysis [28]. *Note:* The data from [20,25] have been shifted in temperature by +3°C so that the bulk T_g values match for all datasets.

shown in Fig. 1 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 [32]. Subsequently, evidence for a strongly attractive interaction between the polymer and 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 [33].

As can be seen from the data presented in Fig. 1, 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 [34] and ellipsometry measurements of isotactic PMMA on Al substrates [35] 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 [23]. Items (2) and (3) have been shown to be consistent with the presence of a thin liquid-like layer at the free surface [23]. 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. 1).

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 [36].

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 [36,37], rather than measurements of the average T_g value. In response to this suggestion, Ellison and Torkelson have applied the probe fluorescence technique [29,30] to multilayer films incorporating thin layers which contain small quantities of fluorescent probes (either probe molecules or probe-labeled polymer molecules) [31]. 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 [31]. 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 [23,38] and for other systems using other techniques [4] (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) [39] and dielectric relaxation (DR) spectroscopy [24,25,34,40–42]. 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 [30]. DR spectroscopy was used by Fukao et al. [24,25,40] to study thin films of PS, poly(vinyl acetate) and atactic PMMA. 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 [24]. T_g values determined in this manner decreased with decreasing film thickness in agreement with the results of other techniques (see Fig. 1). 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 [34]. In this study, the temperature dependence of the relaxation time $\tau_\alpha^{\max}$ corresponding to the maximum in the α-relaxation loss peak was fitted to a Vogel–Fulcher function of the form

$$\tau_\alpha^{\max} = A\exp[T_A/(T - T_0)], \qquad (2)$$

where 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. T_g was identified as the temperature at which $\tau_\alpha^{\max}$ 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) [42]. T_g values for the i-PMMA layers were determined by applying an activation energy fine-structure analysis [43] 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 [35]. 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 [20].

2.2. 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 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 [20,44–48]. Data points obtained using transmission ellipsometry for freely standing films of narrow distribution PS for different M_w values within the range $575\times10^3 < M_w < 9100\times10^3$ are indicated with symbols in Fig. 2 [47]. 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 [20,44]. 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 [49]. 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. 2 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

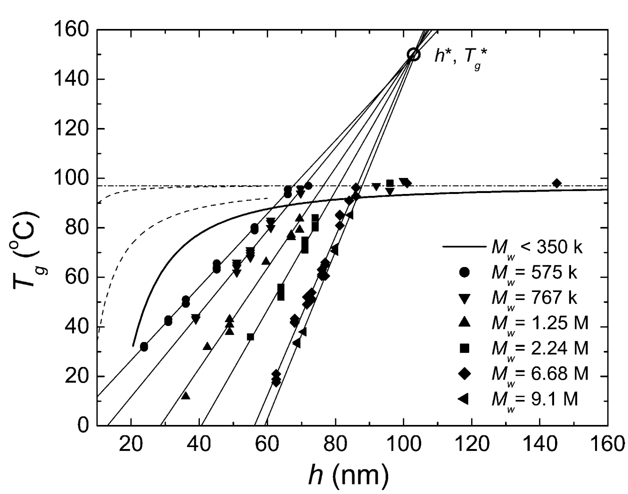

Fig. 2. Glass transition temperature T_g as a function of film thickness h for freely standing polystyrene films of different molar masses. High M_w data, measured using ellipsometry, are displayed using a different symbol for each M_w value [47], and data for $M_w < 350\times10^3$, measured using Brillouin light scattering, are indicated by the thick solid line [46]. The dashed lines for h < 60 nm represent the spread and uncertainty in the T_g data obtained for supported PS films (see Fig. 1). 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.

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 bulk mechanism for sufficiently thin films, resulting in reduced T_g values [36]. de Gennes [36] 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.

For the T_g(h) data in Fig. 2, 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 [19,22]. 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 are 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^*) [47,50]. 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. 2 can be replotted as a universal scaling plot, as shown in Fig. 3. 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. 2 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 [48]. 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. 4. 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 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. 2) [46]. 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 [38]. 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

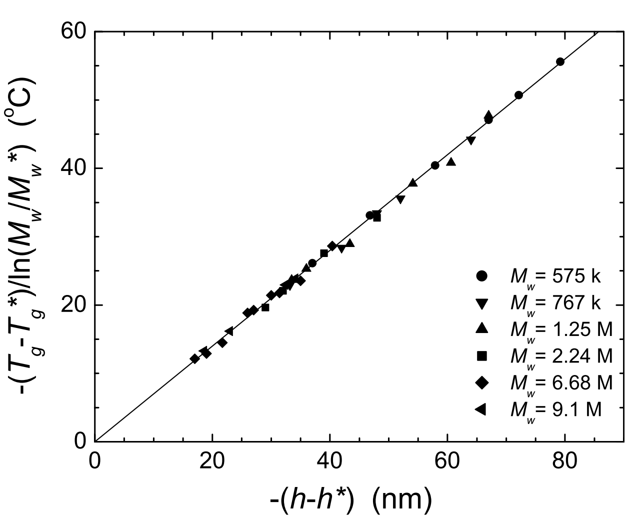

Fig. 3. Scaling plot of all of the reduced T_g values for all molar masses and film thicknesses for the data shown in Fig. 2.

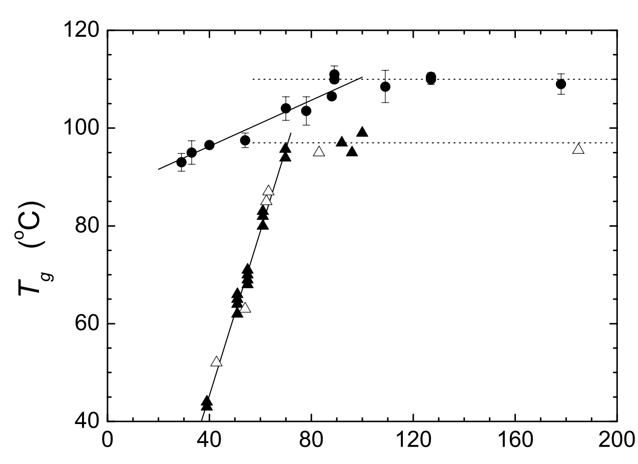

Fig. 4. Comparison of T_g(h) results for freely standing PS films (solid triangles: ellipsometry [47]; open triangles: Brillouin light scattering [20]) and PMMA films (solid circles: ellipsometry [48]) of nearly equivalent molar masses: $M^w = 767 \times 10^3$ for PS and $M_w = 790 \times 10^3$ for a-PMMA.

dependent thicknesses that scale with temperature in the same manner as the cooperativity length scale [38].

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. 2) 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 [4]. It is reasonable to compare these 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 a sufficient signal using 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 Section 3.2 below).

3. 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 [51]. 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.

3.1. *Diffusion in thin polymer films*

The first measurements of in-plane chain diffusion were carried out by Frank et al. [52] using fluorescence recovery after patterned photobleaching (FRAPP) using fluorescently labelled PS molecules. 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 [53]. Although the average concentration of dye molecules in the films is low (0.6–3% by mass), segregation of the dye molecules to the free surface results in much larger concentrations which could artificially enhance the measured diffusion in the near-surface region.

There have been considerably more studies of diffusion perpendicular to the plane of the film. Fluorescence nonradiative 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 [54]. 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) [55,56], and for freely standing PS films incorporating short dPS chains as probe molecules [57]. 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 [55,56], or indistinguishable from that in bulk for freely standing PS films incorporating probe molecules [57]. Neutron reflectometry was used to measure diffusion perpendicular to the film plane for the interface in dPS/hPS bilayer films [58], 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. [59] have recently used dynamic SIMS and neutron reflectometry to study the interdiffusion of the interface in hPS/dPS bilayer films. 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} [60].

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 (see [9])? 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 [6]. 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.

3.2. 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 [61]. 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 [62,63], or repulsive, which enhances the stability of the films [61]. Unsupported or freely standing polymer films are always unstable to the formation and growth of holes at elevated temperatures [64–66], since the dispersion interaction is always attractive for this film geometry which is symmetric about the midplane of the film [61]. 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 $R_c = h/2$ [67]. 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 [68].

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 [69–72]. The importance of nonlinear viscoelastic effects in interpreting these experimental results has also been considered [73–75].

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 [47]. Hole formation and growth in freely standing films was first measured using optical microscopy [64,66], 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 [66], it was found that τ decreased with decreasing film thickness h. This result was interpreted in terms of the bulk phenomenon of shear thinning [76] 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 [77]. 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 analysed to obtain the characteristic growth time τ [77]. 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. 5. The T_g values of the freely standing PS films were 97 (bulk value), 66 and 25 °C for films with $h = 91$, 68 and 51 nm, respectively [47]. Unfortunately, τ can be obtained only for a limited range of temperatures, since measurements of the characteristic growth time τ are limited by the rapid growth

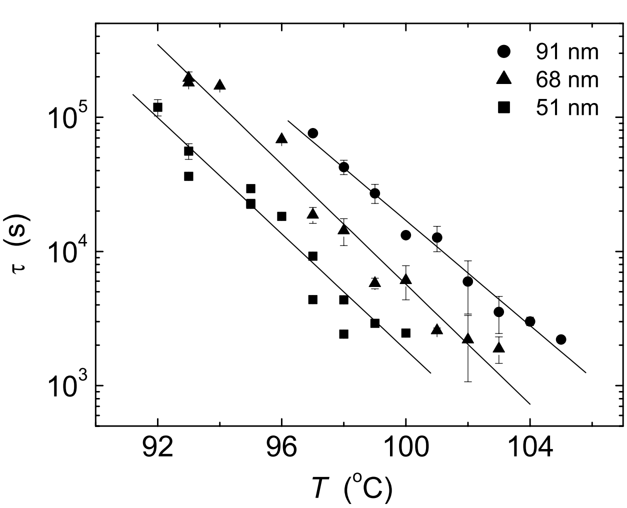

Fig. 5. Characteristic growth time τ as a function of temperature T for the growth of holes in freely standing PS films of three different thicknesses with $M_w = 2240 \times 10^3$ as measured using a differential pressure experiment [77].

of holes at temperatures $T > T_g^{bulk}$. The small shifts in temperature between the different data sets shown in Fig. 5 can be explained in terms of the bulk phenomenon of shear thinning [66,77]. 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.

4. Discussion and summary

We have described considerable experimental evidence that shows that segmental mobility can be enhanced in very thin polymer films while the motion of entire chains is unchanged from that in bulk. In particular, the results obtained for freely standing polymer films are unique and remarkable, with very large reductions in the glass transition temperature and no corresponding enhancement of whole chain motion for very thin films. Several ideas have been proposed to resolve this apparent contradiction [9]: a variation in mobility across the thickness of the films, differences in the polymer mobility parallel and perpendicular to the plane of the films, and decoupling of segmental and chain motions in thin polymer films. 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. Another key issue centres on the length scale over which changes in mobility can be observed, and the fluorescently tagged multilayer films studied in [31] hold much promise to elucidate more completely the detailed T_g behaviour near free polymer surfaces and within thin polymer films. The nonequilibrium nature of thin polymer films, which are produced by spincoating techniques and cannot be fully annealed at temperatures greater than T_g due to the inherent instability discussed in Section 3, is a potential concern since spincoating can produce radial alignment and reduced entanglement of the polymer chains with corresponding anisotropy in the physical properties. However, recent studies have shown that possible reductions in entanglement density in spincoated polymer films are not responsible for T_g reductions in thin polymer films [26,78].

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. In addition, computer simulations and theoretical models have been developed to learn in detail about the structure and dynamics of confined glassy liquids. A recent discussion of the free surface experiments, the computer simulations and the theoretical models is given in [9].

Considerable progress has been achieved in understanding the effect of the film interfaces and free surfaces on the glass transition and whole chain motion. 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.

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