

Some insights into the structural relaxation of spin-cast, glassy polymer thin films

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The widespread use of thin films in a range of applications and industries, from coatings, inks and lithography to nano-imprinting, optoelectronics, and memory devices ¹, has made the understanding of thin films, particularly the changes induced by structural relaxation and solvent evaporation, very important. There is a need to know if a film will change in dimensions after its deposition and how fast these changes will occur. Physical ageing of thin polymer systems is, more generally, an important phenomenon in polymer physics: when a polymer is cooled quickly below its glass transition temperature (T_g) at which point freezing of the matrix takes place ², it is in a non-equilibrium state. When it is aged at temperatures below T_g , a structural relaxation towards the equilibrium volume can take place ^{2 3}. (The equilibrium volume represents the volume obtained through infinitely slow cooling.) Recent works have shown that the structure, wetting, and mobility of polymers in thin films can differ greatly from those of the bulk ^{3 4 5}. For example, a well-documented property of thin polymer films that exhibits thickness dependence is its T_g ^{6 7}.

In many applications, thin films are prepared by depositing a dilute solution of polymer onto a substrate; then the substrate is spun at high velocity during which the solution spreads, thereby ejecting any excess off the substrate⁸. Subsequently during this process, as

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solvent evaporates, the polymer volume fraction, ϕ_{pol} , increases while at the same time the T_g of the solution also increases and approaches the experimental temperature. When the solution's T_g reaches the experimental temperature, the solution forms a glass. The film is then in a state of non-equilibrium, the structure having been 'frozen in.'^{3,9} This current work concerns the relaxation that occurs in polymers that have undergone such a "solvent quench," rather than a thermal quench, through the glass transition.

Two poly(butyl methacrylate) polymers have been used in our study: P(normal-BMA) and P(tertiary-BMA). These isomers have a large difference in their T_g values, while their repeat unit's elemental compositions are identical and therefore differences in interactions with solvent or silicon substrate are not expected to affect the experiments. P(norm-BMA) has a T_g of 20 °C¹⁰, which is below the experimental temperature that is *ca.* 23 °C: therefore it remains rubbery throughout the experiments. In contrast, P(tert-BMA) has a T_g of 107 °C, below which the polymer forms a glass and is subject to relaxation. Hence, P(tert-BMA) and P(norm-BMA) films were used to explore the differences between rubbery and glassy behaviour.

The polymers were provided by Polymer Source Inc. (Quebec, CA) and were used as received. The number average molecular weights (M_n) of the two polymers were comparable, being 182 kg/mol for P(norm-BMA) (polydispersity (M_w/M_n) of 1.02) and 138 kg/mol for P(tert-BMA) and $M_w/M_n = 1.06$. In all experiments, thin films were deposited by spin-casting solutions in toluene at a rate of 2000 rpm and for a time duration of 30 sec. The substrates were single-crystal (100) silicon wafers, used as received such that the native oxide was on the surface. Film thickness was kept constant at 130 nm to minimize thickness effects. Films were aged at room temperature (23 °C) under vacuum for different periods of time up to 24 hours, to allow solvent to leave the film and for the structures to relax.

Ellipsometry measurements (VASE, J.A. Woollam Co., Lincoln, NE, USA) were taken as a function of time over multiple wavelengths, selected to provide the greatest sensitivity. The film samples were placed on the ellipsometer stage previously fitted with a heating stage (Linkam, Surrey, UK). During the measurements, films were heated in air at a constant rate set to 2 °C min⁻¹ from room temperature (~23°C) to a maximum of 150 °C (chosen to avoid any thermal decomposition of the polymer¹¹). The films were then cooled at an equal but opposite rate of -2 °C min⁻¹. The ellipsometric angles Ψ and Δ were measured as a function of time. Fitting of the data using a Marquardt algorithm was performed to obtain the

thickness, h , and refractive index, n , of the film as a function of time. Time was correlated to temperature through the heating rate. The fitting parameters were the thickness, h , and the parameter A of the refractive index in the Cauchy dispersion model^{8,12}, $n(\lambda) = A + \frac{B}{\lambda^2}$, where B is a material constant and λ is the wavelength of the incident light.

Relaxation processes are normally observed in bulk polymers by measuring the volume of the glass, V_t , at a given time. The relative departure from the equilibrium volume, δ_V , is then defined as $\delta_V = (V_t - V_\infty)/V_\infty$, where V_∞ represents the equilibrium volume obtained after long relaxation times². In an analogy to bulk behaviour, the relaxation in thin films can be monitored by measuring the thickness of the glass, h , at a given time (and temperature). A final equilibrium value for the thickness, h_∞ , is obtained from a film after heating and cooling to room temperature. Its value is obtained from ellipsometry in a full spectroscopic scan from 400 nm to 800 nm. It was found that the thickness changes occurring over time after a heating-cooling cycle were negligible in comparison to what was found during the cycle. The relative departure from equilibrium, defined as the excess thickness normalised with respect to h_∞ at room temperature, was calculated as $\delta_{RT} = (h - h_\infty)/h_\infty$. In these experiments in which temperature is not constant, δ_{RT} also contains information on the thickness increase arising from thermal expansion. Using a measurement of the initial film thickness after spin-casting, h_0 , the *initial* departure from equilibrium thickness, δ_0 , can be defined as $\delta_0 = (h_0 - h_\infty)/h_\infty$.

Figure 1 shows the variation of δ_{RT} as a function of the temperature for the P(norm-BMA) isomer (top figure), which is a rubbery polymer at room temperature. The linear thermal expansion coefficient $\alpha = 1/h(\partial h/\partial T)_{P,t}$ was calculated from a linear fit to measurements of thickness as a function of temperature.

Figure 1.

A value of $\alpha = 7.3 \times 10^{-4} \text{ K}^{-1}$ was obtained, which agrees with the literature value¹⁰ of $7.0 \times 10^{-4} \text{ K}^{-1}$. (Note that if thermal expansion is restricted in the plane of the film, one would expect to see a higher expansivity in the direction normal to the plane¹³. Thus, in this materials system, there is no evidence that an attraction between the polymer and substrate is

preventing slippage of the polymer along the substrate). It was found that the thickness dependence on temperature was essentially identical during the heating and cooling stages. There is no evidence for structural relaxation, as is expected for a rubbery polymer. The superposition of the heating and cooling curves supports the conclusion that the rubbery polymer retains no solvent, which would lead to a volume change upon its liberation. This result clearly agrees with the ideas proposed by Leibler and Sekimoto¹¹ that an important factor in solvent retention in polymers must be the increase in bulk modulus of the polymer as it undergoes transition from rubbery to glassy phase. They proposed that the chemical potential of the solvent in a polymer solution should be modified from the standard Flory-Huggins expression when the polymer becomes a glass, adding an additional term, which is a function of the polymer bulk modulus.

On the other hand, Figure 1 (bottom part) shows temperature dependant data obtained from P(tert-BMA), having a T_g of 107 °C, that is well above room temperature. Initially, as the temperature rises, the film exhibits a thermal expansion that is broadly consistent with the literature values for a polymer glass expansion coefficient.

If the film contained no solvent, we would expect the rising trend to continue until it approached the T_g of the neat polymer glass at which point the expansivity would increase towards that of the rubbery state. However, this is clearly not the case, as the film's expansion is arrested when reaching $47 \pm 3^\circ\text{C}$, which is interpreted as being an apparent glass transition temperature (arrow in the figure) of the glassy polymer matrix. If we consider that there is some solvent trapped in the polymer matrix, then below this temperature, the solvent is unable to leave the film as this would require a compression of the matrix (assuming no voids are allowed to be created because of the associated rise in surface energy). According to the Kelley-Bueche polymer/solvent description¹⁴ the presence of solvent (with a low T_g) in a polymer depresses its T_g as a function of the amount of solvent present^{14,15}. When this lower glass transition temperature is reached, the distortion energy^{2,15} is overcome and trapped solvent is released, allowing the film to decrease in thickness while at the same time raising further the polymer/solvent T_g . During this period both phenomena compete: thermal expansion increases the thickness while solvent loss is decreasing it. Upon re-heating the film in a second cycle (data not shown), the thermal expansivity follows the same paths for the glassy and rubbery states that were observed in the first cooling curve. This result indicates that relaxation and accompanying solvent loss are complete after the initial heating.

These differences in relaxation and expansion behaviour observed between the glassy and rubbery polymers have not been demonstrated explicitly in thin films in any previous work that we have seen.

Figure 1 shows clearly this period as expansion is arrested until temperatures approaching the bulk T_g of the polymer. Cooling data shown in Figure 1 can accurately be used to calculate values such as the T_g of the neat polymer (112 ± 3 °C calculated, 107 °C literature value¹⁰), and thermal expansion coefficient of the glassy phase ($\alpha_g = 2.0 \times 10^{-4}$ K⁻¹ calculated, $\alpha_g = 2.80 \times 10^{-4}$ K⁻¹ literature value) and the rubbery phase ($\alpha_r = 7.4 \times 10^{-4}$ K⁻¹ calculated, $\alpha_r = 7.20 \times 10^{-4}$ K⁻¹ literature value)¹⁰. Sufficiently good agreement with the literature values contributes to our confidence in interpreting the data obtained.

Consideration of the relative departure from equilibrium, δ , is best suited for isothermal experiments. In order to gain an insight into the temperature dependence of the fractional “excess volume,” beyond the equilibrium volume, a better approach is to calculate the departure from equilibrium thickness at a given temperature relative to the equilibrium thickness at that same temperature as $\delta(T) = [h(T) - h_\infty(T)] / h_\infty(T)$. In this case, the h_∞ values were taken from the cooling curve. When $\delta(T)$ is plotted as in Figure 2, it is seen that it is unchanged until reaching a certain temperature (47 °C), at which point the film is able to relax. This finding is consistent with the idea that the concentration of solvent in the film lowers its T_g from that of the neat polymer. Only at the apparent glass transition temperature, does $\delta(T)$ start to decrease. We can use the apparent glass transition temperature to obtain the solvent concentration required in the film to depress the temperature from the bulk value. To lower the glass transition temperature to 47 ± 3 °C, the solvent volume fraction needs to be 0.140 ± 0.011 . (This calculation assumes a value for the T_g of toluene taken as 2/3 of the crystal melting temperature and uses the Kelley-Bueche polymer/solvent equation¹⁴.)

Figure 2.

Follow-on experiments were carried out to examine the relaxation processes in blends of P(tert-BMA) and PMMA. Three different P(tert-BMA):PMMA blend ratios of 9:1, 1:1 and 1:9 were measured. Samples were aged in vacuum for different times at room temperature prior to analysis. The departure from room temperature equilibrium, δ_{RT} , was measured with

ellipsometry when the system was heated at a constant rate of $2\text{ }^{\circ}\text{C min}^{-1}$ for blends with ageing times ranging from 0 to 96 hours. Figure 3 shows, as an example, δ_{RT} as a function of the temperature for the P(tert-BMA):PMMA blend with a ratio of 1:9 for a range of times aged in vacuum at room temperature. When the films are heated above an apparent T_g , there is a structural relaxation leading to a decrease in film thickness. Once the film has fully relaxed and reached equilibrium at the experimental temperature, the thickness starts to increase again, as is expected according to its thermal expansivity. When the film is aged for longer, the departure from equilibrium and the amount of relaxation decrease.

Figure 3.

Little or no change is appreciable as the ageing time is increased both for pure P(tert-BMA) and for P(tert-BMA):PMMA with a ratio of 9:1 (data not shown). The results differ strongly for PMMA-rich films with a P(tert-BMA):PMMA ratio of 1:1 and 1:9. We observe in freshly-cast (non-aged) films, that as the fraction of PMMA is increased in the blend, the film exhibits a higher initial departure from its equilibrium. When a film is aged at room temperature, the structural relaxation occurs - albeit very slowly - prior to the heating of the film. Hence, the amount of relaxation observed as the film is heated decreases with increasing aging time. This concept explains why volume relaxation is greatly affected by the temperature of the system¹⁶ and the time of ageing. Similar behaviour has been observed in many studies in the literature on bulk polymers,^{2 17 16} but few reports have explored these phenomena in thin film systems¹⁸. The data seem to suggest that P(tert-BMA)-rich films relax very fast during the deposition procedure, such that they obtain an equilibrium thickness soon after the deposition. In contrast, PMMA films undergo a significant amount of slow relaxation.

Further analysis was used to identify differences between the polymers. A volume relaxation rate, β , can be defined in terms of the slope of isothermal measurements of δ as¹⁶ $\beta = d\delta/d\log(t-t_0)$, where t_0 is initial time, t_i is the time at point i, and δ is as defined previously. This relaxation rate can be compared for the different systems to get some insight into the relation between the isothermal relaxation rate and the compositions of the different polymer blends. For each of the compositions, the gradient of δ (obtained isothermally at room temperature) plotted against the logarithm of time was used to obtain a value of the isothermal relaxation rate, β , at room temperature. The measurements of β and δ_0 for these different systems are reported in Table 1.

Table 1

Looking at the trend in β , it is apparent that PMMA-rich films exhibit the largest values compared to the other compositions. As the ratio of P(tert-BMA) increases in the blend, the relaxation rate decreases considerably, reaching the point where the film is pure P(tert-BMA) and in which the relaxation rate is the lowest. The initial departure from equilibrium is lowest for P(tert-BMA) and increases with increasing PMMA fraction. The fact that P(tert-BMA) has the lowest δ_0 and also exhibits almost no relaxation for over a period of several days suggests that P(tert-BMA) films hold much less solvent after spin-casting from dilute solution than PMMA rich films do. These differences are surprising considering that PMMA and P(tert-BMA) have similar glass transition temperatures and bulk moduli.

This difference in relaxation characteristics between the polymers may stem from differences in selective character of the solvent and not from the mechanical properties of the polymers, which are similar. The χ parameter determines how the chemical potential varies with ϕ_{pol} ¹⁸. The χ parameter for the P(tert-BMA) /toluene system, for a polymer volume fraction of 0.8 is around 0.25-0.3^{19,20,21}, similar to the PS/toluene system, while for PMMA/toluene the value is higher, at around 0.45^{10,19,20}. One can argue that if the chemical potential is higher (as is the case for the toluene/PMMA) and when there is some solvent in the vapour phase - such as during the spin-casting process - it will be thermodynamically favourable to have more solvent in the polymer solution. Our results are consistent with this expectation for the toluene/PMMA case in comparison to toluene/ P(tert-BMA) or toluene/PS²². Despite its non-selective character, toluene is a better solvent for the P(tert-BMA) than the PMMA.

In conclusion, the film's initial conformation after a solvent quench was explored for different polymers and their blends. In spin-cast rubbery P(norm-BMA) films, there is no evidence for structural relaxation upon heating and no evidence for remnant solvent. On the other hand, spin-cast glassy P(tert-BMA) films undergo structural relaxation above an apparent T_g . Comparisons between glassy P(tert-BMA) and PMMA/P(tert-BMA) with different blend ratios have shown a strong dependence of both the initial departure from equilibrium thickness, δ_0 , and the relaxation rate, β , on the P(tert-BMA) content of the film. These results indicate that P(tert-BMA)-rich films could be losing solvent and forming dense films much faster than PMMA-rich films, such that they are closer to their equilibrium thickness when

first deposited. On the other hand, the rate of structural relaxation in the solid P(tert-BMA) film is significantly slower than in PMMA. This result shows that P(tert-BMA) forms films with a high thickness stability, something that is attractive in practical applications, such as lithography and emerging nano-imprinted coatings.²³

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Figures captions:

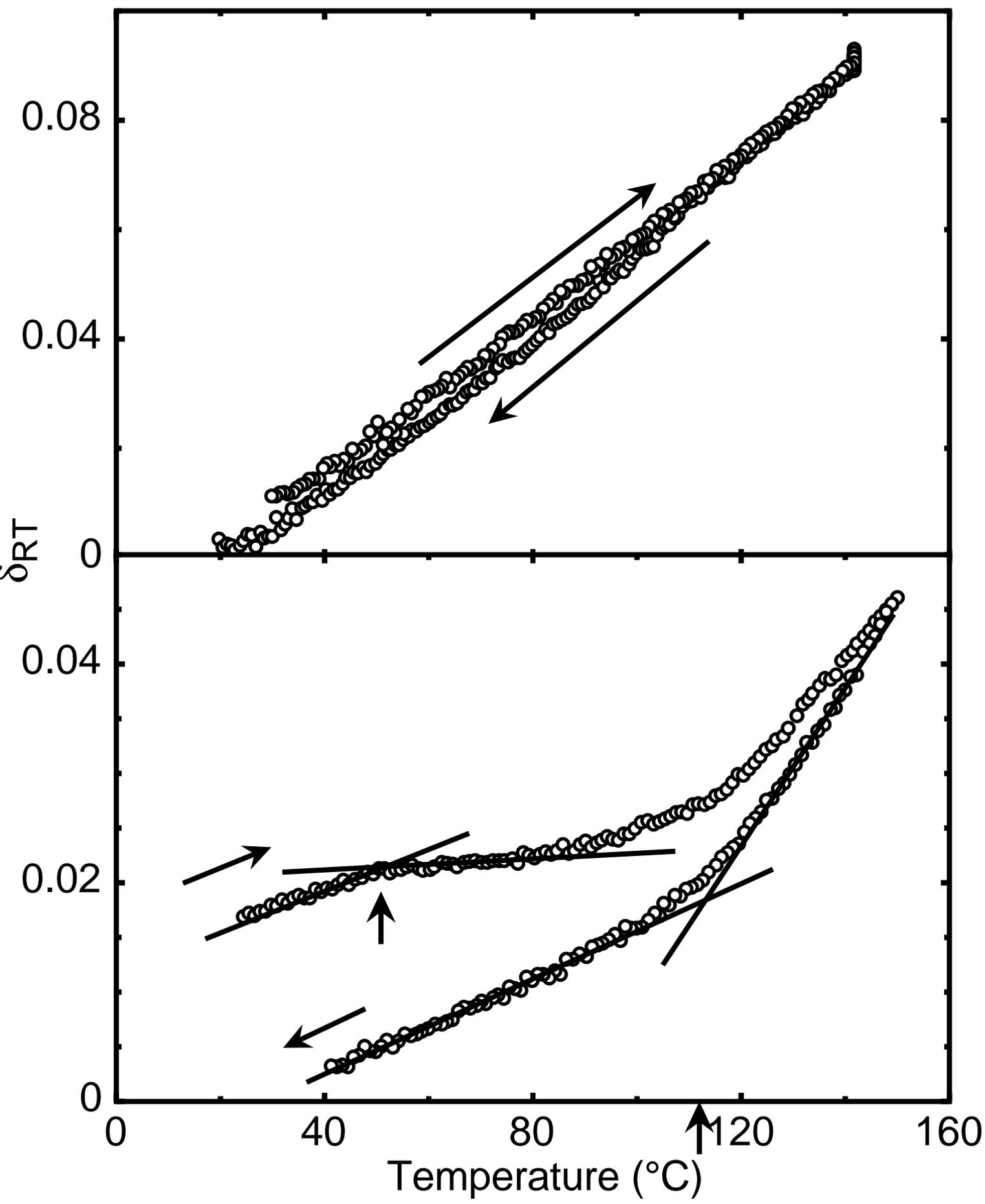
Figure 1 – The relative departure from room temperature equilibrium, δ_{RT} , as a function of temperature. Top: P(norm-BMA) film heated from room temperature to 130°C at 2 °C min⁻¹ then cooled to room temperature at the same rate. No glass transition is seen at any temperature and heating and cooling curves almost overlap perfectly. Bottom: The same type of data obtained from a glassy P(tert-BMA) film shows a departure from linearity and large difference between the heating and cooling curves. The apparent T_g on cooling is indicated by an arrow.

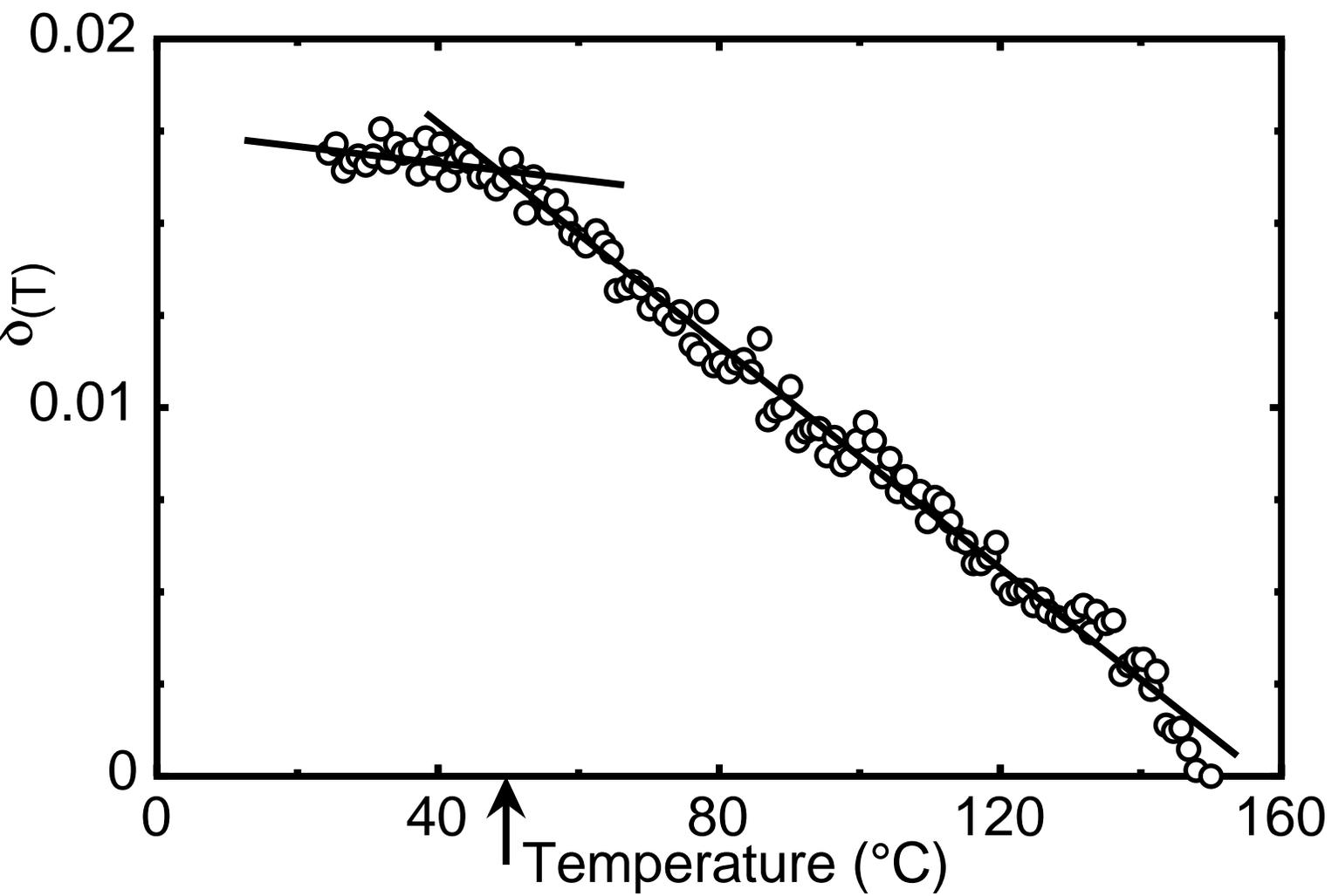
Figure 2 – The temperature-dependence of the relative departure from equilibrium thickness (corrected for temperature), $\delta(T)$, for a P(tert-BMA) thin film. It can be clearly seen that $\delta(T)$ remains constant until reaching 47 °C. At that temperature the film starts to relax, seen as a decrease in $\delta(T)$. One interpretation is that it has reached its apparent glass transition temperature.

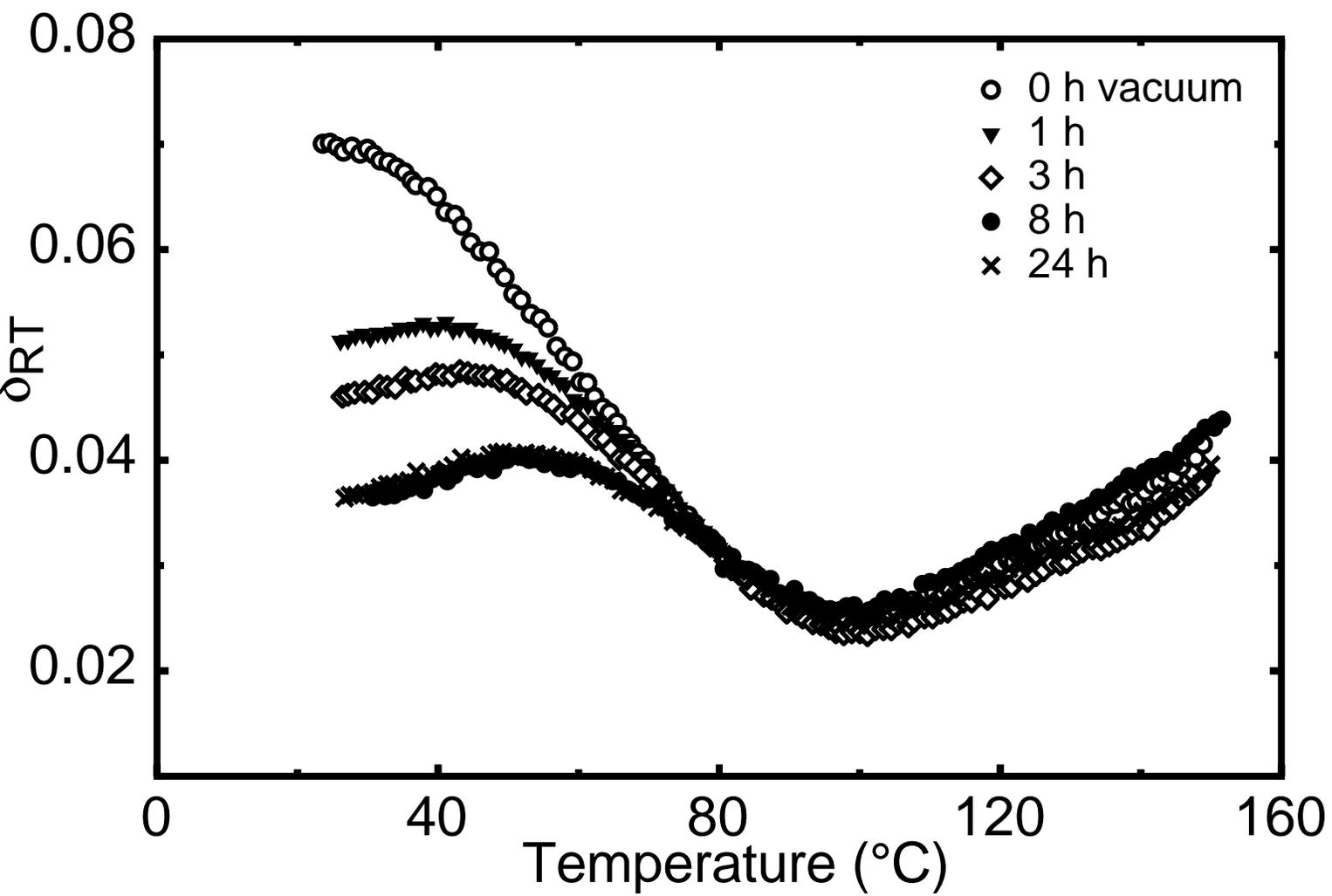
Figure 3: The relative departure from equilibrium, δ_{RT} , as a function of T . Heating curves are shown for P(tert-BMA):PMMA (1:9 ratio) blend films aged in vacuum over a range of times.

Table 1. Thermal Expansivity and Initial Departure from Equilibrium Thickness Values for Homopolymers and Polymer Blends

Polymer system	$\beta(K^{-1})$	δ_0
Pure PMMA	198×10^{-4}	0.0992
PMMA 9:1 P(tert –BMA)	113×10^{-4}	0.0700
PMMA 1:1 P(tert –BMA)	66×10^{-4}	0.0391
PMMA 1:9 P(tert –BMA)	7×10^{-4}	0.0200
Pure P(tert -BMA)	5×10^{-4}	0.0169







The structural relaxation of glassy, spin-cast thin polymer films was investigated using spectroscopic ellipsometry. Results from poly(*tert*-butyl methacrylate) (P(*tert*-BMA) and poly(*norm*-butyl methacrylate) (P(*norm*-BMA) polymers and also blends of P(*tert*-BMA) and poly(methyl methacrylate) (PMMA) are compared. It is found that P(*tert*-BMA) films exhibit almost no relaxation over a period of several days, in comparison to PMMA-rich films, which exhibit significant amounts of relaxation. Blends show intermediate amounts of relaxation.

