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Notes

Entanglement and the Molecular Weight Dependence of Polymer Glass Transition Temperature

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The effect of molecular weight (MW) and the chain end on the glass transition temperature, T_g, of a polymer is an old subject of research interest. The results were often analyzed in terms of an empirical equation of the form[1,2]

$$T_g = T_\infty - m/M_n \qquad (1)$$

which was based on the idea of excess free volume of the chain ends over that of a similar unit within the chain. In so doing, the anisotropy of free-volume distribution along the polymer chain contour is averaged out.

The relationship between the temperature dependence of viscosity and T_g is often expressed in terms of the well-known Williams–Landell–Ferry equation.[3] In general, viscosity is a product of a friction constant and a structural factor. The structural factor is basically independent of temperature. Thus, T_g is much related to the friction constant of the polymer chain segment. Chain entanglement imposes a topological constraint effect on the motion of the polymer chain; namely, the polymer chain follows a reptation process.[4-11] Thus, it would not be surprising to see that entanglement has an effect on the MW dependence of T_g. As shown below, this effect leads us to an entirely new way of looking at the polymer system. It is suggested and supported by data that the normalized MW (M/M_e, where M_e is the entanglement MW), at which T_g starts to be sensitive to the change of MW, is a universal constant ($\sim$10). Another transition point occurring at M_e was pointed out before.[11] It will be briefly discussed here again.

On the basis of the Doi–Edwards theory, a general stress relaxation function containing four dynamic processes has been obtained for an ideal monodisperse case as[9]

$$G(t) = (4\rho RT/5M_e)[1 + \mu_A(t/\tau_A)][1 + (1/4)\mu_X(t/\tau_X)][B\mu_B(t/\tau_B) + C\mu_C(t/\tau_C)] \qquad (2)$$

where $\mu_A(t/\tau_A)$ is the Rouse motion of an entanglement strand (assuming entanglement points fixed in the short time region), $\mu_X(t/\tau_X)$ the chain slippage through entanglement links, $\mu_B(t/\tau_B)$ the primitive chain-length fluctuation, and $\mu_C(t/\tau_C)$ the reptational motion corrected for the chain length fluctuation effect. Each relaxation time (τ_A, τ_X, τ_B, and τ_C) is given by a product of a frictional factor, K, and a structural factor. The theoretical forms of the different relaxation processes and the MW dependencies of the structural factors of the relaxation times are referred to in previous papers.[9-11] K is given as

$$K = \zeta b^2 N_0^{\,2}/kT\pi^2 M^2 \qquad (3)$$

where ζ, b, and M/N_0 are the friction constant, length, and mass associated with each Kuhn segment. K can be considered as equivalent to the friction constant in all the following discussions.

The zero-shear viscosity, η_0, and steady-state compliance, J_e, calculated from eq 2 explain very well the MW dependence of η_0 and J_e and their respective transition points, M_c and M_c'.[9,11] In terms of eq 2, the line shapes of the linear viscoelastic spectra of a series of nearly monodisperse polystyrene samples have been very successfully analyzed quantitatively.[9,10] Very significantly, it was found from the line-shape analyses that the K value in the $\mu_X(t)$, $\mu_B(t)$, and $\mu_C(t)$ processes is independent of MW to MW as low as 1.24 M_e, while the K value in the $\mu_A(t)$ process (denoted as K') is affected by the change of MW. K'/K has a plateau value of 3.3 in the high MW region ($M >$ 130 000) and decreases to a limiting value of 1 as decreasing MW approaches M_e. The results are reproduced in Figure 1. It has been proposed that for $K' > K$ the friction constant for the polymer chain segment to move in the direction perpendicular to the chain contour is higher than that along the chain contour.[9,10] This explanation is consistent with the idea that a certain local extra free volume is associated with the polymer chain ends. In the motions along the chain contour, as one segment moves, the next segment along the chain follows in and so on. The chain end segments with extra free volume should take the lead and contribute to the mobility of the motions along the chain contour. By this mechanism, the extra free volume at chain ends is in effect always available to the processes along the chain contour. On the other hand, the portion of this extra free volume available to the $\mu_A(t)$ process of a polymer chain depends on the concentration of free chain ends of polymer molecules surrounding it. Thus, the K' values extracted from the line-shape analyses are MW dependent. Furthermore, the K'/K value approaching the value of 1, as MW approaching M_e, supports this explanation.[10] $K' > K$ indicates anisotropic free-volume distribution along the polymer chain. The observed T_g of a bulk polymer material is the average effect of the anisotropic free-volume distribution. In the conventional ways of studying T_g effects, the anisotropy in general cannot be observed. In his creep measurements of nearly monodisperse polystyrene samples and poly(vinyl acetate) samples, Plazek[12] observed that between T_g and T_g + 25 °C the time-scale shift factor varied more rapidly with temperature in the glass–rubber transition region (the $\mu_A(t)$ process region, where K' is applicable) than in the terminal region (the $\mu_B(t)$ and $\mu_C(t)$ processes, where K is applicable). Plazek's observation implies that K' be greater than K, in agreement with our results. As also indicated by Plazek's results, K'/K is expected to be independent of temperature above T_g + 25 °C. Our K'/K values were obtained at 127.5 °C for polystyrene (T_g = 100 °C).

Since K' is the only friction constant that changes with MW above M_e as shown in Figure 1, any MW dependence of T_g in the region of $M > M_e$ should have a correspondence to the MW dependence of K'. K' starts to become sensitive to MW when MW is below $\sim$130 000 ($M/M_e \approx 10$, M_e = 13 500 using $M_e = 4\rho RT/5G_N$ for calculation[10]) for polystyrene. In about the same region, we should see the

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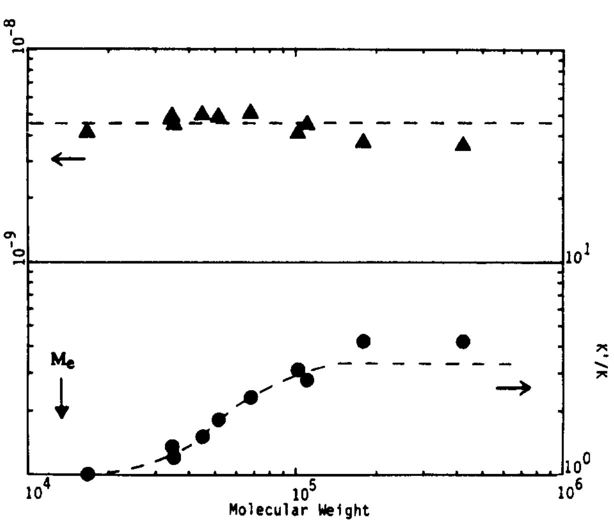

Figure 1. K and K'/K values obtained as a function of MW from the line-shape analyses of the measured linear viscoelastic spectra of a series of nearly monodisperse polystyrene samples. The dashed line in the high MW region (the plateau region) is the K'/K value corrected by 30% to the obtained data values for a molecular weight distribution effect (see ref 10 for the details). The K'/K value becomes dependent on MW when MW is below ~130 000. This figure is reproduced from ref 10.

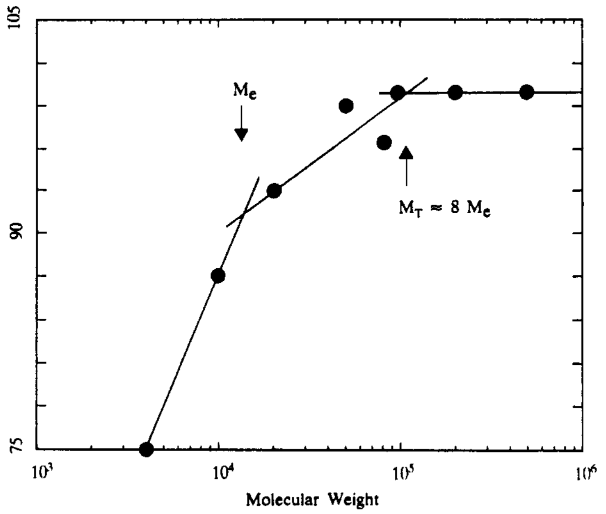

Figure 2. MW dependence of the glass transition temperature, T_g, of nearly monodisperse polystyrene samples; data obtained by Rudin and Burgin.[13]

effect of MW change on T_g begin to occur. Indeed, this is what the literature data have indicated. Shown in Figure 2 is the MW dependence of T_g of the nearly monodisperse polystyrene samples obtained by Rudin and Burgin.[13] Above MW ~110 000 ($M/M_e \approx 8$), T_g is independent of MW. Below MW ~110 000, the effect of MW or chain ends on T_g becomes quite noticeable. (We define the MW at this transition point as M_T). In view of the possible error involved in the K'/K and T_g determinations, it is quite satisfactory to observe the M_T value to be within 10 ± 2 M_e.

While the T_g data of Rudin and Burgin clearly show the beginning of the MW dependence of T_g at $M_T \sim 10 \pm 2\ M_e$, the number of data points is somewhat less than one hopes to see. Thus, independent T_g measurements of a series of nearly monodisperse polystyrene samples (17 samples) have been undertaken. The samples were obtained from TSK (Toyo Soda Manufacturing Co., Japan) and Polysciences, Inc. Those samples from Polysciences were washed by the process of dissolution/filtration/precipitation and thoroughly dried in vacuo before being used for DSC measurements. The T_g data of the polystyrene samples measured with DSC at the rate of 2 °C/min are shown in Figure 3 with those of Rudin and Burgin (adjusted by moving all data values up 1 °C). Since we are only interested in the change of the T_g values with MW, the zero rate data are not really needed. There is a good agreement between the two sets of data. Including two sets of data, the M_T value is determined to be ~11 M_e, which is well within the expected 10 ± 2 M_e range.

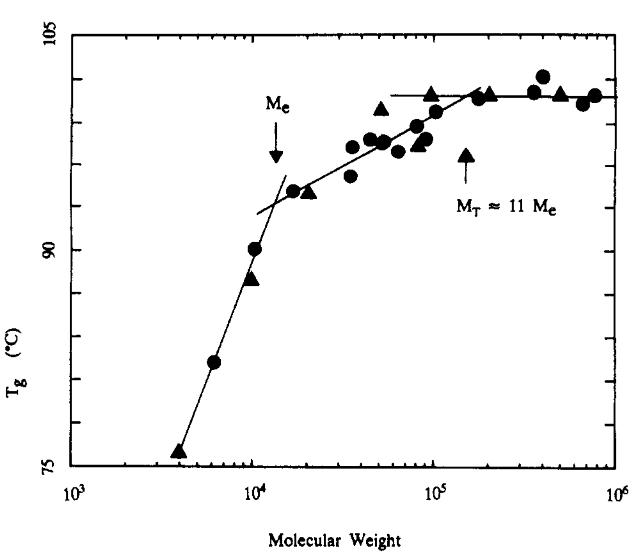

Figure 3. MW dependence of the glass transition temperature, T_g, of nearly monodisperse polystyrene samples: (▲) data obtained by Rudin and Burgin[13] (all data points are moved up by 1 °C); (●) present data measured at the rate of 2 °C/min.

It has been shown that the general linear viscoelastic theory, which was used in the line-shape analyses of the viscoelastic spectra, is universal as the MW is normalized with respect to the entanglement MW, M_e. The general theory is shown to be equally applicable to the concentrated polymer solution systems, which are made up of a high MW nearly monodisperse polystyrene component ($M_H > M_e$) and a low MW one being too short to entangle ($M_L < M_e$, as the solvent).[14] In the concentrated polystyrene solution case, the K'/K ratio values follow the same curve obtained for polystyrene melts, as the MW is normalized with respect to the entanglement MW (M_e for melts and $M_e' = M_e W_H^{-1}$ for concentrated solutions where W_H is the weight fraction of the high MW component) in both cases. These results suggest that the normalized MW dependence of K'/K be universal and be extendable to flexible linear polymers other than polystyrene. Then, we expect that M_T/M_e be a universal constant.[19]

In Figure 4, the T_g data of polybutadiene as a function of MW obtained by Colby et al.[15] are shown. The data were obtained for polybutadiene samples with ~9% vinyl. The entanglement MW of these samples has been determined to be 1480 (using $M_e = 4\rho RT/5G_N$ for calculation).[15,16] At around MW = 8 M_e, one can observe the beginning of decrease of T_g with decreasing MW for polybutadiene. This transition point is within the expected narrow range of the M_T value. The M_e values of polystyrene and polybutadiene differ by about 1 order of magnitude and so do their M_T values. In other words, M_T and M_e are strongly correlated as expected from universality of the MW dependence of K'/K.

Another transition point of the MW dependence of T_g is at M_e. As shown in a previous report,[11] the anisotropy of the free-volume distribution on the polymer chain begins to appear at ~M_e(+) like a "phase" transition. Below M_e, the viscosity of the polymer melt drops precipitously with

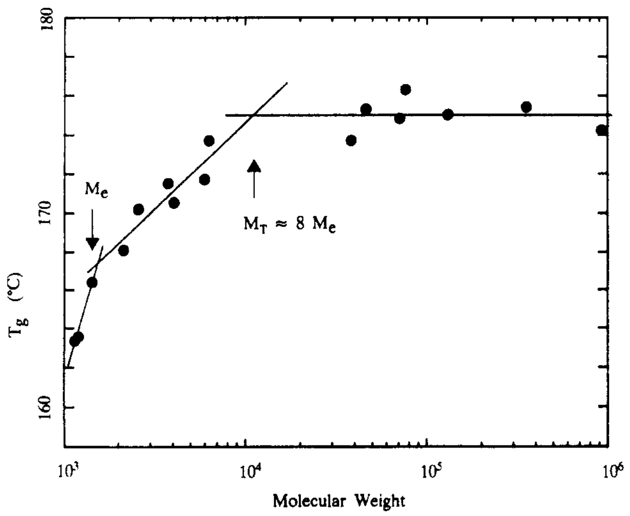

Figure 4. MW dependence of the glass transition temperature, T_g, of nearly monodisperse polybutadiene samples; data obtained by Colby, Fetters, and Graessley.[15]

decreasing MW. This is mainly due to absence of entanglement for MW < M_e, where the increase of the free volume with decreasing MW has a direct effect on viscosity. For MW > M_e, the K value being independent of MW has a *buffering* effect on the free volume and T_g change with MW as observed through the zero-shear viscosity measurements. (See refs 11 and 16 for more details of the buffering effect.) As reflected by the ratio of the viscosity values measured at two different temperatures (see Figure 2 of ref 18),[17,18] this effect is also observable in the MW dependence of T_g directly measured with a DSC. As clearly observable in Figures 2–4, T_g begins a sharper drop with decreasing MW at M_e.

In summary, because of the topological constraint effect caused by chain entanglements, T_g of nearly monodisperse polymers shows two clear transition points: one at $10 \pm 2\ M_e$ and the other at M_e. The former is associated with the beginning of K' to be sensitive to the change of MW and the latter with the disappearance of the topological constraint effect with decreasing MW.

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