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Does the Molecular Weight Dependence of T_g Correlate to M_e?

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ABSTRACT: The nature of the molecular weight (MW) dependence of the glass transition temperature (T_g) in polymers still remains a subject of discussion. Recently, Hintermeyer et al. [*Macromolecules* 2008, *41*, 9335] proposed that the MW at which the dependence of T_g saturates corresponds to the molecular weight between entanglements, M_e. We demonstrate on the example of four polymers that there is no relationship between M_e and saturation of the molecular weight dependence of T_g.

It is well-known that the glass transition temperature (T_g) in linear polymers depends strongly on their molecular weight (MW). At not very low MW, the molecular weight dependence of T_g is usually described reasonably well by the empirical Fox−Flory equation $T_g(M_n) = T_g(\infty) - K/M_n$, where K is a material dependent parameter and $T_g(\infty)$ is the asymptotic value of T_g at infinitely high MW.[1] This dependence has been explained in the framework of the chain-end free volume approach and in the framework of the Gibbs-DiMarzio theory.[2] Recently, T_g(MW) has been related to the chain statistics.[3] In all of these cases T_g is assumed to be a smooth function of MW. However, in 1975 Cowie[4] suggested that the T_g(MW) may have three different regions: (i) at very low MW T_g varies nearly linear with log(M_n) up to some MW_1; (ii) above MW_1 the T_g exhibits a much weaker but still linear variation of T_g with log(M_n) up to some MW_2; and (iii) T_g is independent of molecular weight when MW > MW_2. A recent paper by Hintermeyer et al.[5] came back to the idea proposed by Cowie. The authors presented very accurate analysis of the dielectric relaxation time in three polymers: polystyrene (PS), polydimethylsiloxane (PDMS) and polybutadiene (PB). The molecular weight dependence of T_g, fragility and Vogel−Fulcher−Tammann (VFT) parameters were analyzed and a few interesting observations were reported. The molecular weight at which T_g saturates, MW_2, was discussed and it was suggested that MW_2 can be related to the molecular weight between entanglements, M_e. On the basis of this suggestion, Hintermeyer et al.[5] concluded that chain dynamics might modify glassy dynamics. This point may be crucial for understanding whether or not entanglements influence segmental dynamics.

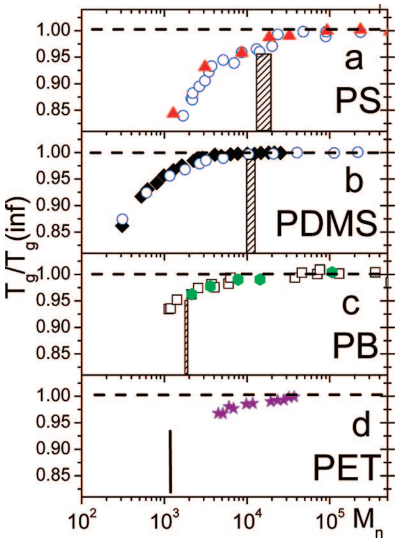

Figure 1. Molecular weight dependence of the glass transition temperature in (a) PS (○, data from Hintermeyer et al.,[5] ▲, Santangelo et al.[6]); (b) PDMS (○, Hintermeyer et al.,[5] ◆, Clarson et al.[7]); (c) PB (□, Colby et al.,[8] ⬢, Kisliuk et al.[9]) and (d) PET (★, Montesserat et al.[10]). Dashed line indicates asymptotic value of $T_g(\infty)$ (372.6 K[5] and 374 K[6] for PS; 144.5 K[5] and 149.8 K[7] for PDMS; 174.7 K[8] and 180.7 K[9] for PB; 342.4 K[10] for PET). The different values of $T_g(\infty)$ obtained for the same polymer in different sources might be related to the different procedures used to estimate T_g. The difference in behavior of $T_g(M_n)$ in PDMS might be related to larger polydispersity of short chains used by Hintermeyer et al.[5] Shaded area indicates the range of M_e values[13−15] for the presented polymers. Only one source[13] was found for the value of M_e in PET.

The main goal of the present Note is to test the idea suggested by Hintermeyer et al.[5] of the relationship between molecular weight at which the dependence of T_g saturates and M_e. The literature data for T_g(MW) was analyzed for the same three polymers used by Hintermeyer et al.[5] with an additional example of poly(ethylene terephthalate) (PET) included (Figure 1). The PS data was taken from Hintermeyer et al.[5] (obtained by dielectric spectroscopy - DS) and Santangelo et al.[6] (obtained by differential scanning calorimetry (DSC), at 10 K/min rate). The PDMS data was taken from Hintermeyer et al.[5] (DS) and Clarson et al.[7] (DSC, 10 K/min rate). The PB data was taken from Colby et al.[8] (DSC, extrapolated to zero heating rate) and Kisliuk et al.[9] (DSC, 10 K/min rate). The PET data was taken from Montesserat et al.[10] (DSC, 10 K/min rate). Hintermeyer et al. mentioned that the microstructure of the PB samples analyzed varied from 6% to 20% vinyl content. It is known that vinyl content affects the value of T_g drastically, from $T_g(\infty)$ ~ 175 K in 1,4-PB to ~270 K in 1,2-PB.[11,12] In particular, a change in microstructure alone from 6% to 20% vinyl content leads to a change in T_g ~ 15 K,[11,12] the value is almost as large as the entire variation of T_g with MW in PB presented by Hintermeyer et al.[5] (~25 K). It means the data of Hintermeyer et al. was affected by both MW and microstructure and we believe that this is the reason for their difference with other literature data. To avoid this complication, T_g(MW) data from two other sources[8,9] was used, where the PB samples had well controlled microstructure (vinyl content ~6−9%). These two data sets were obtained on two independently synthesized series of PB and agree well with each other (Figure 1c).

We emphasize that Figure 1 presents the T_g(MW) for all four polymers in the same scale $T_g/T_g(\infty)$ from ~0.8 up to ~1.04. This allows for a more accurate comparison of the T_g(MW) behavior in the different polymers, including PS (where T_g changes by a factor of 2) and PDMS (where T_g variations are ~15%).

We used the values of M_e estimated using traditional mechanical measurements. Comparison of three different sources[13−15] gives scattering of the M_e values ~35% for PS, ~20% for PDMS and less than 10% for PB. They are shown

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as shaded areas in Figure 1. Unfortunately, only one source was found for the value of M_e in PET.[13]

Analysis of the T_g(MW) data for these four polymers (Figure 1) suggests that there is no correlation between the molecular weight at which the dependence of T_g saturates (MW_2) and M_e. For example, $T_g(M_n)$ saturates in PS at MW ≈ 30 000−100 000 g/mol, while it saturates in PDMS already at MW ≈ 8000 g/mol (Figure 1, parts a and b). This indicates that MW_2 in these two polymers differs by a factor of 4−10, while both polymers have approximately the same $M_e \approx$ 12 000−13 000 g/mol.[13] In contrast, $T_g(M_n)$ in PDMS and PB saturates at approximately the same MW ≈ 8000 g/mol (Figure 1, parts b and c), while their M_e's differ by more than 6 times ($M_e \approx$ 1800 in PB[13]). The most obvious case is presented by PET; it has the lowest value of $M_e \approx$ 1170 g/mol among the polymers studied here,[13] while its T_g(MW) does not saturate even at MW ≈ 37 000. Therefore, MW_2 in PET is much higher than in PB although its M_e is smaller. It appears that MW_2 in PET might be similar to MW_2 in PS, although their M_e's differ by 1 order of magnitude.

As was already mentioned, the idea of discontinuous dependence of $T_g(M_n)$ has been proposed by Cowie.[4] Although Cowie did not have as accurate data as presented by Hintermeyer et al., he analyzed 8 polymers. According to the analysis presented by Cowie (Figures 1 and 3 of his paper[4]), MW_2 increases with the increase of $T_g(\infty)$ value. This seems to be consistent with the current analysis (Figure 1) where the molecular weight dependence in low T_g polymers (PDMS and PB) saturates at lower MW than in high T_g polymers (PS and PET). However, it is inconsistent with the idea suggested by Hintermeyer et al.,[5] because $T_g(\infty)$ does not correlate with M_e. For example, PS and PDMS have approximately equal $M_e \approx$ 12 000−13 000 g/mol, but their $T_g(\infty)$ values differ by more than a factor of 2 (Figure 1). Also, $T_g(\infty)$ of PET (342 K) is much higher than $T_g(\infty)$ of PDMS and PB, but yet it has the smallest $M_e \approx$ 1170 g/mol.

The presented analysis clearly demonstrates that there is no relationship between the molecular weigh dependence of T_g and M_e. The latter is usually related to packing length of the polymer,[13] or to "effective chain thickness".[16] Apparently these parameters are not important for the segmental dynamics. Based on the observation that high T_g polymers seem to have higher MW_2, we speculate that the backbone rigidity and bulkiness of the side-groups (parameters that control T_g in polymers[17]) might control the molecular weight dependence of the glass transition temperature. It was proposed[3] that chain statistics (related to the chain rigidity) might affect the molecular weight dependence of T_g because it affects chain packing and sample density. When chains approach Gaussian behavior, the molecular weight dependence of density and T_g saturate.[3] Unfortunately, this analysis has been performed only on two polymers, PDMS and PS, and it is not clear whether it is applicable to other polymers.

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