QUANTITATIVE EVALUATION OF THE GIBBS-DIMARZIO THEORY OF THE GLASS TRANSITION FOR POLYSTYRENE

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ABSTRACT

The applicability of the Gibbs-DiMarzio (G-DM) theory of the glass transition ($T_g$) is quantitatively evaluated for polystyrene (PS). The analysis was conducted under the assumption that both the inter- intramolecular energy ratio ($r$) and the effective chain segment density ($n$) remain constant while the fractional free volume at $T_g(V_o)$ varies as a function of the reciprocal degree of polymerization ($10^3/\bar{P}$). Based upon reduced parametric plots of $T_g/T_{g_\infty}$ versus $10^3/\bar{P}$, the results showed that the G-DM equations were satisfactory for PS; when $0.015 \leq V_o \leq 0.045$, optimum agreement occurred at $n = 1.80$, $r = 1.05$.

INTRODUCTION

Over the past 30 years a number of theories have been developed to account for the variation in the glass transition temperature ($T_g$) of polymeric materials as a function of molecular weight (MW). Three of the most notable of these approaches have included the straight line technique of Fox and Flory$^1$ and the statistical mechanical theories of Gibbs$^2$ and Gibbs-DiMarzio$^3$ (G-DM). Because of the universal applicability claimed for the latter approach, the G-DM theory has received considerable attention.$^4$-$^7$

Recently Kusy and Greenberg$^6$ introduced a reduced variables technique which simplified the use of the rather unwieldy statistical mechanical equations. Subsequent expansion of this work in terms of the inter- intramolecular energy ratio ($r$) and the fractional free volume at $T_g(V_o)$ explicitly characterized the functional dependence
of each of these parameters on MW. In addition, an index (n) which related the effective number average of chain atom segments (x) per degree of polymerization (P) was incorporated into the reduced variable equations in order to better account for structural differences among polymers. By assigning reasonable values to the parameters n, r and Vo, the theoretical predictions of the statistical mechanical equations were compared with Tg data obtained from the literature for four well documented polymers. Qualitative assessment of these results suggested that the G-DM theory adequately described the PMMA, PS and PVC cases but was unsuccessful for POMS.

Because of the complexities inherent in a theory which incorporates multifunctional dependencies, further examination has indicated that a qualitative evaluation is not sufficient to establish the validity of a particular approach. Recently a statistical analysis technique was utilized in a comparison of the Gibbs theory with experimental results obtained for PMMA, and the advantages of such a quantitative determination were clearly demonstrated. The present effort applies these quantitative analytical techniques to the PS data set in order to make an unbiased assessment of the G-DM theory.

THEORETICAL DEVELOPMENT

The system of equations which comprises the G-DM theory has been presented in detail elsewhere. However, the approach can be summarized by consideration of the following two equations:

\[
\frac{2\beta \exp \beta}{1+2\exp \beta} = \ln \left[1+2\exp \beta \right] = \frac{-x}{x-3} \left[ \frac{1}{1-V_o} \ln \left( V_o + (1+V_o) \ln \left( \frac{x+1}{2xV_o} + 1 \right) \right) + \frac{\ln(3(x+1))}{x} \right]
\]

\[
\beta = -\frac{1}{r} \left[ \ln V_o - 2 \ln \left( \frac{2xV_o}{2xV_o + (x+1)(1-V_o)} \right) \right] \left[ \frac{(x+1)(1-V_o)}{2xV_o + (x+1)(1-V_o)} \right]^{2}
\]

Here \( \beta \) is a dimensionless parameter equal to \(-\epsilon/kT_g \) where \( \epsilon \) is the flex energy and \( k \) is Boltzmann's constant. In accordance with the assumption that \( V_o \) decreases monotonically with decreasing MW, equations (1) and (2) can be solved iteratively by maintaining nP and r constant while simultaneously varying \( V_o \) until a unique \( \beta \) derived.