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A theory of the molecular-mass dependence of glass transition temperatures for polydisperse homopolymers

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Arbitrary distributions of finite molecular-mass homopolymers are treated as one-phase solutions of chain ends and high polymers in order to derive an entropic relation for the dependence of their glass transition temperatures on the number-average degree of polymerization. Absolute predictions of this equation from high molecular-mass and dimer properties are found to be in good agreement with dilatometric transition temperatures for polystyrene. The theoretical equation is generalized to allow for the characterization of chain ends by properties other than those of dimers. An initial approximation to the entropic expression is obtained by neglect of the difference between chain-end and high-polymer transition increments of heat capacity. Two subsequent approximations arise from a series expansion of logarithmic functions. In order of decreasing accuracy these three approximations are: a new form of the Ueberreiter–Kanig equation, a logarithmic expression, and a new form of the Fox–Flory relation.

1. Introduction

The dependence of glass transition behaviour on degree of polymerization for an homologous series of polymers presents a problem of technological interest in connection with the handling and end-use conditions of polymeric materials. Fundamental aspects of the phenomenon are of intrinsic scientific concern within the general topic of number-dependent transitions. Equations presently used to describe the effect of molecular mass on glass transition temperatures derive principally from three sources: dilatometric studies of volume–temperature relations as a function of molecular mass [1, 2], associated theoretical discussion [1–6], and the Gibbs–DiMarzio statistical thermodynamic theory for equilibrium properties of amorphous polymers [7]. Based upon dilatometric data for polystyrene (PS), Fox and Flory [1] proposed a linear dependence of T_g on reciprocal degree of polymerization, n^{-1}. This dependence can be derived from the free-volume hypothesis of glass formation in conjunction with some primary assumptions about the contribution of chain ends to specific volume [1, 4–6], and also from the assumption that a principle of corresponding states can be applied to the effect of molecular mass on glass transition temperatures [8]. Further, a theory for the glass transition as an outcome of chain-segment restriction due to van der Waals forces and counteractive thermal scissoring motion [9] gives results consistent with the Fox–Flory relation, although limitations of the model make it inappropriate for the low molecular-mass region. Experimental evidence and theoretical discussion in support of the Fox–Flory relation is generally limited to intermediate molecular masses and above: a dilatometric study of PS fractions to very low molecular masses by Ueberreiter and Kanig [2] gives data better fit by a linear relation between T_g^{-1} and n^{-1} [2, 3].

The Ueberreiter–Kanig dependence, found acceptable from the dimer to high-polymer range, can be interpreted formally as a chain-end free-volume effect [2–4] and in terms of a corresponding states principle [8]. In turn, both of the above mentioned dependences differ from an equation

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derived from the configurational entropy theory of glass formation [7], although the Gibbs–DiMarzio transcendental relation and the Ueberreiter–Kanig expression give a roughly similar non-linear dependence of T_g on n^{-1}.

Both the Fox–Flory and Ueberreiter–Kanig equations in present form require dilatometric data for their use. Consequently, they are not convenient predictive expressions. Separately, calculation of glass transition temperatures from the Gibbs–DiMarzio equation requires a value for the energy difference between low-lying rotational isomeric states (flex energy), the variation of this property with degree of polymerization [10], and the free-volume fraction at glass transition temperatures, taken as independent of chain length. In practice, the flex energy is usually approximated as constant and its value inferred from the theoretical relation (fit to the experimental high-polymer transition temperature) for a suitably chosen free-volume fraction*.

Difficulties such as those touched on in the preceding discussion suggest the need for a theoretical clarification of the relation between glass transition temperatures and molecular mass, leading to predictive equations for the effect in terms of properties accessible to direct and convenient experimental measurement. Outlined below is a phenomenological theory intended to meet some of these needs.

2. Theory

The glass transition in general appears to be consistent with a change of state at fixed entropy and volume with finite increments in certain first derivatives of these variables. Properties necessary for use in an entropic theory, such as transition temperatures and transition increments of heat capacity, can be measured conveniently in automated calorimetric devices; consequently, theoretical relations for the effect of molecular mass on glass transition temperatures are derived here from the entropy of a polydisperse system. For convenience, the isobaric transition in linear homopolymers is considered.

An arbitrary overall distribution, characterised by the number of molecules n_i with degree of polymerization i, can be considered a mixture of chain ends and units with properties of the high-polymer limit. Chain-end and high-polymer properties are distinguished below by the respective superscripts e, o. Associated entropies of mixing are indicated by superscripts m, and their molecular-mass dependence referred to by subscripts i. The entropy, S, per mol of mers can then be written as the sum

$$S = \frac{\Sigma n_i(i-2)S^0}{\Sigma i n_i} + \frac{2\Sigma n_i S^e}{\Sigma i n_i} + \Sigma \Delta S_i^m. \qquad (1)$$

Provided the chemical constitution of chain ends is closely related to that of other mers, the excess functions ΔS_i^m will be given by perfect solution (random mixing) formulae. As the distribution of molecular masses is fixed, these random mixing properties are consequently unchanged at T_g. This simplification noted, chain-end (dimer) and high-polymer glass transition temperatures T_g^e, T_g^0 and their corresponding transition increments ΔC_p^e, ΔC_p^0 are defined. These definitions, the condition that glass transitions are continuous in the entropy, and approximation of heat-capacity transition increments as temperature-independent combine to provide the equation

$$\ln T_g = \frac{\Delta C_p^0 \ln T_g^0 \dfrac{\Sigma n_i(i-2)}{\Sigma n_i} + 2\Delta C_p^e \ln T_g^e.}{\Delta C_p^0 \dfrac{\Sigma n_i(i-2)}{\Sigma n_i} + 2\Delta C_p^e} \qquad (2)$$

This expression for the glass transition temperature of a general distribution as a function of number-average degree of polymerization, in effect an "average molecule" representation, can be rewritten in terms of the number-average molecular mass, $\bar{M}_n$, the mass per mer, m_1 (here approximated as identical for chainend and interior mers) and specific transition increments of heat capacity as

$$\ln T_g = \frac{\Delta C_p^0 \ln T_g^0 \bar{M}_n + 2m_1(\Delta C_p^e \ln T_g^e - \Delta C_p^0 \ln T_g^0)}{\Delta C_p^0 \bar{M}_n + 2m_1(\Delta C_p^e - \Delta C_p^0)} \qquad (3)$$

A discriminating initial test of Equations 2 and 3 is afforded by a comparison of calculated and experimental glass transition temperatures for well-characterized distributions made up of polymers with substantial differences between dimer and high-polymer transition properties. The result of such a comparison, for narrow fractions of polystyrene and their binary blends, is given in Fig. 1. Calculated and experimental values of T_g are in satisfactory agreement.

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*The semi-empirical flex energy so determined has been discussed in some generality in [11].

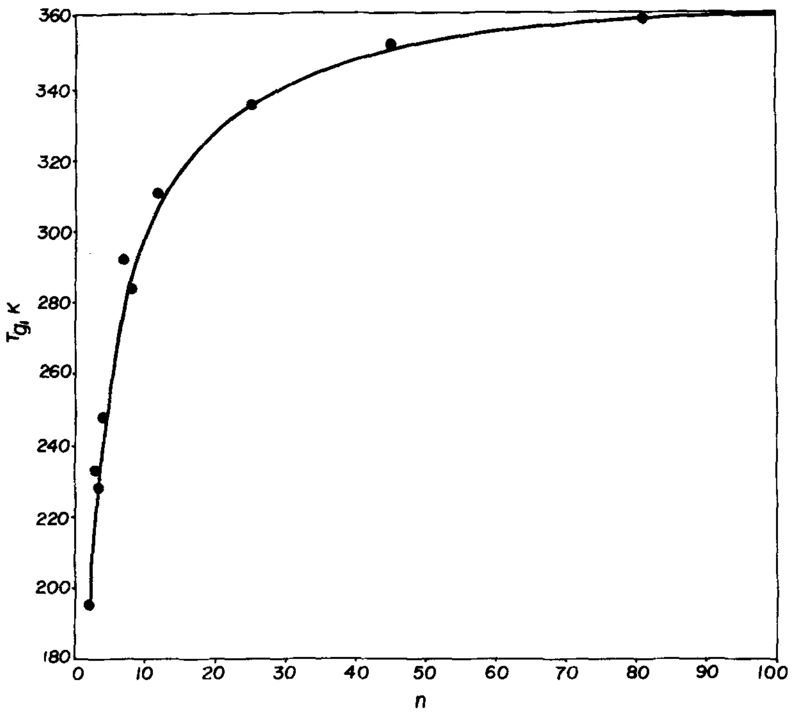

Figure 1 The dependence of glass transition temperatures, T_g, on degree of polymerization, n, for polystyrene. Dilatometric transition temperatures reported by Ueberreiter and Kanig [2] are shown as filled circles. The predictions of Equation 2 are shown as the curve. Data for Equation 2: $T_g^e = 195$ K, $T_g^0 = 371$ K [2]; $\Delta C_p^e/\Delta C_p^0 = 2.05$ [12].

Polymers for which dimer properties are either unavailable or not readily accessible to measurement can be included in the theory by a straightforward extension of the derivation leading to Equation 2. For a compatible mixture of chain ends, degree of polymerization $k(>1)$, and mers with high-polymer properties, the glass transition temperature is given by

$$\ln T_g = \frac{\Delta C_p^0 \ln T_g^0 \dfrac{\Sigma n_i(i-k)}{\Sigma n_i} + k\Delta C_p^k \ln T_g^k}{\Delta C_p^0 \dfrac{\Sigma n_i(i-k)}{\Sigma n_i} + k\Delta C_p^k} \qquad (4)$$

where

$$\Delta C_p^k = \frac{(k-2)\Delta C_p^0 + 2\Delta C_p^e}{k} \qquad (5)$$

and, as before, transition increments of heat capacity are per mol of mers. As it stands, Equation 4 can be used to interpolate between T_g^0 and T_g^k and, also, to extrapolate from T_g^k to T_g^e. Similar conditions apply to general distributions of the homopolymer.

The effect of molecular mass on transition increments of heat capacity can be considered a secondary influence on the chain-length dependence of glass transition temperatures. Consequently, a physically based first approximation to Equation 4 can be obtained by neglect of the difference between ΔC_p^0 and ΔC_p^k. The relation between T_g and number-average degree of polymerization, $\bar{n}$, is then

$$\ln T_g = \left(1 - \frac{k}{\bar{n}}\right) \ln T_g^0 + \frac{k}{\bar{n}} \ln T_g^k. \qquad (6a)$$

Secondary approximations to Equation 4 follow from a series expansion of a rearranged Equation 6a, or use of the binomial theorem for the equivalent relation

$$T_g = T_g^0 \left(\frac{T_g^k}{T_g^0}\right)^{\frac{k}{\bar{n}}}. \qquad (6b)$$

Consistent use of reference transition temperatures as denominators for a single-term expansion of each ln function leads directly from the rearranged Equation 6a to the dependence of reciprocal glass transition temperatures on $\bar{n}$ found by Ueberreiter and Kanig [2, 3]. This Equation,

$$\frac{1}{T_g} = \frac{1}{T_g^0} + \frac{k}{\bar{n}} \left(\frac{1}{T_g^k} - \frac{1}{T_g^0}\right), \qquad (7)$$

identifies the Ueberreiter–Kanig constant in terms of k-mer and high-polymer properties. A similar expansion of the ln functions with T_g, as denominator, leads to the following form of the Fox–Flory [1] equation

$$T_g = T_g^0 - \frac{k}{\bar{n}}(T_g^0 - T_g^k). \tag{8}$$

Again, calculation of the relevant constant requires only two transition temperatures and the chain-end degree of polymerization.

The relative accuracy of Equations 6 to 8 with respect to their common origin can be established by some minor algebra in conjunction with conditions on the ratios $\Delta C_p^e/\Delta C_p^0$ and T_g^0/T_g^e. In the absence of a substantial mass deficiency of chain-end mers with respect to their interior counterparts, both ratios would generally exceed unity. As a consequence, for all finite $\bar{n} > k$, glass transition temperatures predicted by Equation 6 would be above those calculated from Equation 4. Transition temperatures given by the modified Ueberreiter–Kanig equation would be between those of Equations 4 and 6. The modified Fox–Flory relation would give values of T_g greater that those of Equations 4 to 7. Therefore, the most accurate of the three approximations to Equation 4 would be Equation 7 followed by, in order of precedence, Equations 6 and 8. This result resolves a largely unacknowledged conflict between the functional form of the Ueberreiter–Kanig equation and that of the Fox–Flory equation in favour of the former, although this does not preclude the possibility of rather small quantitative differences between the predictions of these expressions and their antecedents for certain limited ranges of $\bar{n}$. The compensatory nature of the two formal approximations necessary for the derivation of Equation 7 from Equation 4 can be significant; for PS the Ueberreiter–Kanig constant is 4.87×10^{-3} K^{-1} (T_g^0 and T_g^e from [2]), in good agreement with the curve-fit value of 4.96×10^{-3} K^{-1} [3].

3. Conclusions

The prediction of glass transition temperatures for homopolymer systems of arbitrary polydispersity by means of the theory given here is a straightforward and relatively convenient exercise. Four properties are necessary for the primary relation: high-polymer and chain-end transition temperatures and their corresponding transition increments of heat capacity. It is not strictly necessary that these properties be known for monodisperse systems, although for brevity the formal discussion has been given in terms of actual rather than average high-polymer and chain-end properties. Prompted in part by the present lack of data on chain-end heat capacity, approximations to the general relation have been derived. Of these, an equation identical in form to the Ueberreiter–Kanig relation is the most accurate. This equation requires only the high-polymer glass transition temperature and the transition temperature for a polymer of known finite number-average molecular mass. Therefore, two sufficiently separated transition temperatures can serve to predict accurate values of T_g for all $\bar{n} \geqslant 2$.

There are clear connections between the theory presented here and a recent description of composition-dependent glass transition temperatures for multi-component mixtures of compatible polymers [13]. These derive from the tenet that homopolymers of arbitrary molecular mass are in effect one-phase random mixtures of high polymers and chain ends.

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