where

$$\gamma = \{2a/(\sum nP_n) + a^2(\sum P_n)/(\sum nP_n)^2\}(\sum P_n)$$

i.e.

$$\mathrm{DP_w/DP_n} < (\mathrm{DP_w/DP_n})_0$$

since

$$(\mathrm{DP_w/DP_n})_0 > 1$$

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(4) Solutions of these equations were obtained by numerical integration with an automatic computer (VAX 11-780). Some difficulty was encountered because the equations are "stiff", that is, the solutions contain a term that varies rapidly with time. This term arises mainly from the first two equations and corresponds to the rapid reaction of initiator with monomer. After a short time this rapidly varying term becomes small, but its presence nevertheless makes the solutions numerically unstable unless very short time increments are used. We tried several methods of integration, of which the most successful was the method of Gear. Variation of the time steps, $\Delta t'$, affects the numerical results by 1–2%.

(5) The tolerance parameters limits the magnitude of the incremental error at each time increment; however, the overall error, being the resultant from all time increments, is much larger and grows with time.

(6) These statements apply to hypothetical systems of constant volume; i.e., the supply of monomer is assumed not to increase the volume of the system. Such an assumption is approximately justified as long as the investigated solutions of monomer and polymers are dilute.

(7) See the remarks after eq 1–4.

Compositional Variation of the Glass Transition

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ABSTRACT: A relation between differential changes of temperature and pressure is obtained for the glass–liquid boundary of random solutions. On integration, this relation yields predictive equations for the compositional variation of glass-transition temperatures and of glass-transition pressures.

Introduction

A thermodynamic theory for the compositional variation of glass-transition temperatures,[1-7] T_g, has provided a unified basis for several topics within the general theme, for both macroscopic[1,5,7-13] and microscopic[2-7,14] composition variables, X_i. The principal equation of this description is obtained by equating the entropy of the glassy and liquid states, respectively S^g and S^l, and taking definite temperature integrals. As outlined below, a more general and transparent theory can be derived from the equality $dS^g = dS^l$ for the glass-transition boundary as a function of pressure, P, temperature, T, and composition. A relation between differential changes of temperature and pressure is thereby obtained for the composition-dependent glass transition. This new equation can be integrated to give, as special cases, an equation for the compositional variation of T_g and an equation for the compositional variation of the transition variable for the isothermal transition (the glass-transition pressure, P_g). A particular advantage of the differential formulation is that for the compositional variation of T_g and P_g, corresponding pure-component properties, T_{g_i} and P_{g_i}, enter as constants of integration.

Theory

For random mixtures the excess entropy of mixing is essentially combinatorial and independent of temperature and pressure. Consequently, at fixed but arbitrary composition, the differential relation $dS^l = dS^g$ for the glass–liquid boundary can be written as

$$\sum X_i \Delta C_{p_i}\, \mathrm{d} \ln T + \sum X_i \Delta C_{T_i}\, \mathrm{d} \ln P = 0 \tag{1}$$

In eq 1 the ΔC_{p_i} denote pure-component glass-transition increments of heat capacity, the $\Delta C_{T_i} = \Delta(\mathrm{d}S_i/\mathrm{d} \ln P)_T$ denote the isothermal analogues of this property, and $\sum$ denotes the sum over all pure components of the solution. Use of a Maxwell relation gives $\Delta C_{T_i} = -P\Delta(V_i\alpha_i)$, where V_i and α_i are in turn pure-component current volumes and isobaric expansivities, and converts eq 1 to

$$\frac{\mathrm{d} \ln T}{\mathrm{d}P} = \frac{\sum X_i \Delta(V_i\alpha_i)}{\sum X_i \Delta C_{p_i}} \tag{2}$$

Equation 2 includes the pure-component ($X_i = 1$) Ehrenfest relation[15] as a special case.

To derive an expression for the compositional variation of T_g, consider the indefinite integration of eq 1 at fixed pressure, formally

$$\sum X_i \int \Delta C_{p_i}\, \mathrm{d} \ln T = 0 \tag{3}$$

A variety of problems has been addressed successfully by the use of temperature-independent ΔC_{p_i},[1-12] for which eq 3 becomes

$$\sum X_i \Delta C_{p_i} (\ln T_g + a_i) = 0 \tag{4}$$

The constants of integration in eq 4 are obtained from the requirement that at $X_i = 1$, $T_g = T_{g_i}$, to give $a_i = -\ln T_{g_i}$ and

$$\ln T_g = \frac{\sum X_i \Delta C_{p_i} \ln T_{g_i}}{\sum X_i \Delta C_{p_i}} \tag{5}$$

If the ΔC_{p_i} cannot reasonably be approximated as temperature independent,[16] eq 3 together with the boundary conditions can be used to obtain relations for the composition-dependent isobaric transition other than eq 5.

For the isothermal transition, the relation for the compositional variation of P_g for pressure-independent ΔC_{T_i} is

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$$\ln P_g = \frac{\sum X_i \Delta(V_i\alpha_i) \ln P_{g_i}}{\sum X_i \Delta(V_i\alpha_i)} \qquad (6)$$

The theories for the compositional variation of P_g and T_g are evidently parallel in form. Consequently, the entire analysis for the isobaric transition[1-7] can be appropriated for the isothermal transition, with the ΔC_{p_i} and T_{g_i} exchanged for in turn the ΔC_{T_i} and P_{g_i}.

For binary blends an alternative version of eq 2 can be derived from the partial differential equality $(\mathrm{d}T/\mathrm{d}P)_{X_2} = (-\mathrm{d}X_2/\mathrm{d}P)_T/(\mathrm{d}X_2/\mathrm{d}T)_p$ and eq 5 and 6. This, which can be written as

$$\frac{\mathrm{d}\ln T}{\mathrm{d}\ln P} = -\left[\frac{X_1\Delta(V_1\alpha_1) + X_2\Delta(V_2\alpha_2)}{X_1\Delta C_{p_1} + X_2\Delta C_{p_2}}\right]^2 \times \left[\frac{\Delta C_{p_1}\Delta C_{p_2}\ln(T_{g_2}/T_{g_1})}{\Delta(V_1\alpha_1)\Delta(V_2\alpha_2)\ln(P_{g_2}/P_{g_1})}\right] \qquad (7)$$

when compared with eq 2 gives as a consistency condition

$$P = -\left[\frac{X_1\Delta(V_1\alpha_1) + X_2\Delta(V_2\alpha_2)}{X_1\Delta C_{p_1} + X_2\Delta C_{p_2}}\right] \times \left[\frac{\Delta C_{p_1}\Delta C_{p_2}\ln(T_{g_2}/T_{g_1})}{\Delta(V_1\alpha_1)\Delta(V_2\alpha_2)\ln(P_{g_2}/P_{g_1})}\right] \qquad (8)$$

Comment

On the basis of the success of eq 3 (typically in the form of eq 5), the new principal relations (eq 1, 2, and 6—the last of these modified if necessary for pressure-dependent ΔC_{T_i}) should give acceptable predictive descriptions of their particular aspects of the solution glass-transition boundary for miscible blends (including plasticized polymers), molecular weight effects, copolymerization effects, and cross-linking effects.

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Sequence Distribution of Styrene–Butadiene Copolymer Initiated by *n*-Butyllithium

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ABSTRACT: The sequence distribution of styrene–butadiene copolymer initiated with *n*-butyllithium in toluene was investigated by GPC measurements of ozonolysis products in relation to the time–conversion and time–copolymer composition relationships. Rapid increase of conversion and styrene content in the copolymer was observed from about 75% conversion after the consumption of almost all of the butadiene. GPC analysis of the ozonolysis products showed three peaks corresponding to 1–3 styrene sequences flanked by 1,4-butadiene units for the copolymers obtained below 75% conversion. A broad peak due to long styrene sequences was observed in addition to the peaks due to 1–4 styrene sequences for the copolymers obtained above 75% conversion. The average number of styrene units in the long styrene sequence increased from 43 to 65 with increase of conversion from 89% to 100%. The sequence distribution of styrene units determined from the ozonolysis–GPC measurement was in good agreement with that calculated by monomer reactivity ratios.

Introduction

Styrene–butadiene rubber (SBR) is commercially produced by emulsion polymerization or anionic polymerization initiated with alkyllithium. The latter is characterized by the variety of the sequence distribution of styrene units, ranging from almost random copolymers to S–B–S-type triblock copolymers. The sequence distribution can be controlled by the modification of the polymerization conditions, e.g., addition of a polar compound as a randomizing agent, control of the conversion, the controlled charge of styrene and butadiene, or use of a polymer-Li as an initiator to make the block sequence. The approximate distribution of styrene and butadiene units can be predicted from the copolymerization parameters. In practice, however, it seems very difficult to determine the sequence distribution in the case of a partial block copolymer. The occurrence of 1,2 addition of butadiene units may further complicate the situation.

We have proposed a new method for the characterization of the sequence distribution of styrene and 1,2-butadiene

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