Transformation of Liquid to Amorphous Solid: The Time to Vitrify for Styrene Polymerization

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Synopsis

A model is presented for the calculation of the time to vitrify vs. temperature for isothermal polymerization by the chain growth mechanism. The model is based on the glass transition temperature (T_g) rising from its initial value to the reaction temperature. The relationships between T_g and the volume fraction of polymer and monomer, the volume fraction of polymer and the extent of reaction, and the extent of reaction and time are also required. In a plot of temperature vs. time the vitrification curve is generally S-shaped; the time passes through a maximum just above the glass transition temperature of the unreacted monomer and passes through a minimum just below the maximum glass transition temperature. The model applies to linear polymerization in which monomer and high molecular weight polymer are the dominant species, i.e., to chain reactions. In this communication the model is applied to the bulk polymerization of styrene by the free radical mechanism.

INTRODUCTION

The transformation by chemical reaction of low molecular weight liquid into high molecular weight amorphous solid polymer is a fundamental process in the coatings, adhesives, and thermoset industries. As the chemical reaction proceeds, the molecular weight and glass transition temperature (T_g) increase and, if the reaction is carried out below the maximum glass transition temperature (T_{gp}), the T_g will eventually reach the reaction temperature. Vitrification is defined to occur when the glass transition temperature becomes equal to the temperature of reaction. A search of the literature for experimental data reveals that the determination of the time to vitrification has scarcely been studied. The purpose of this report is to extend a model which has been developed for thermosetting systems[1-3] to calculate the time to vitrify for linear isothermal polymerizations. Vitrification is important not only because the material turns to a solid, but because the chemical reaction is quenched and so limiting conversions are reached when reacting below T_{gp}. The limiting conversions obtained at vitrification are also computed. (In practice T_g is generally greater than the cure temperature only because of an inconsistency in the definition of T_g with respect to the quenching of chemical reactions.)

Previous results have shown that in the context of a time–temperature–transformation (TTT) cure diagram for thermosetting materials undergoing step-growth polymerization, the reaction temperature vs. time to vitrification is an S-shaped curve[1,2]. The present work will test the generality of the S-shaped vitrification curve of the TTT diagram by examining a linear system, in particular, the free radical polymerization of styrene. The linear case for step-growth
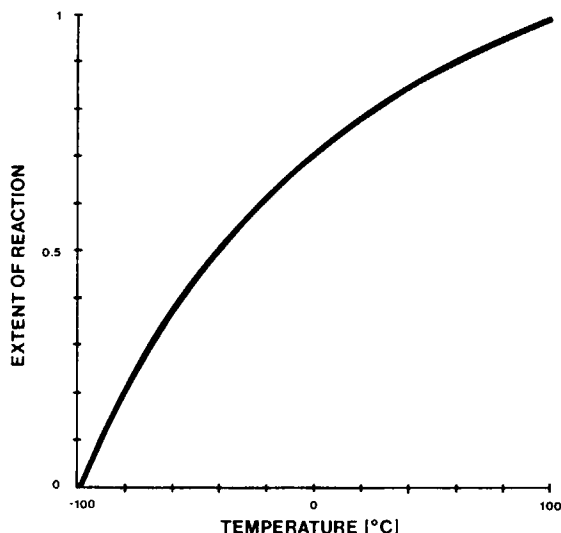
Fig. 1. Extent of reaction at vitrification vs. reaction temperature for linear, free radical polymerization of styrene. See text for model parameters.

polymerization and the nonlinear case for chain-growth polymerization are under investigation.

MODEL

In order to calculate the time to vitrify at a given temperature for linear chain-growth polymerization, several relationships are needed in addition to the criterion that the glass transition temperature equals the temperature of reaction. These relationships are:

(i) T_g vs. volume fraction of polymer;

(ii) volume fraction of polymer vs. extent of reaction; and

(iii) extent of reaction vs. time.

This model differs from previous work[2,3] in that the relationship between T_g and extent of reaction at T_g will be derived from more fundamental concepts, rather than assuming an empirical relationship between T_g and extent of reaction. The conversion at vitrification can be calculated directly from free volume concepts for binary mixtures since in chain polymerization monomer and high molecular weight polymer are the dominant species. Contributions by other species (e.g., initiator) are neglected in this communication.

From free volume theory,[4-6] the glass transition temperature,

$$T_g = \frac{\alpha_p \phi_p T_{gp} + \alpha_m (1 - \phi_p) T_{gm}}{\alpha_p \phi_p + \alpha_m (1 - \phi_p)} \tag{1}$$

where α = difference between the volume coefficients of expansion of liquid and glass, ϕ = volume fraction, and the subscripts p and m refer to polymer and monomer, respectively. Rearranging eq. (1), the volume fraction of polymer,

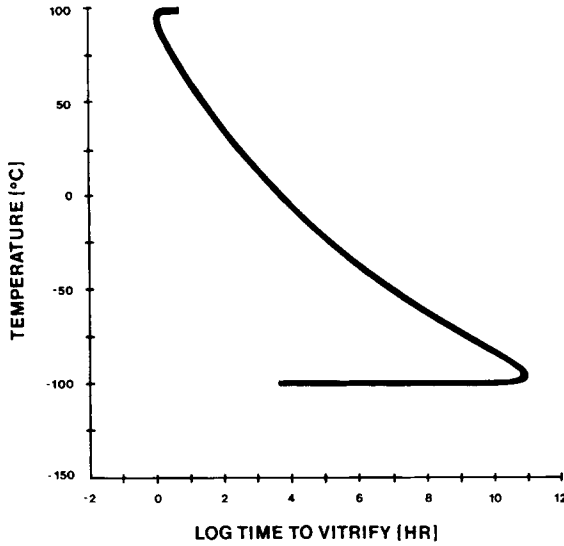$$\phi_p = \frac{\alpha_m (T_{gm} - T_g)}{\alpha_p (T_g - T_{gp}) + \alpha_m (T_{gm} - T_g)} \tag{2}$$

Fig. 2. Reaction temperature vs. time to vitrify for linear, free radical polymerization of styrene: T_{gp} = 100°C, T_{gm} = −100°C (assumed). For other model parameters, see text. Equation (6) is solved from −99.99999995°C to +99.9995°C.

By considering a simple mass balance of monomer and polymer, ϕ_p can be written in terms of the extent of reaction p:

$$\phi_p = \frac{p/\rho_p}{[(1-p)/\rho_m] + p/\rho_p} \tag{3}$$

where ρ = density. This relationship assumes volume additivity for mixtures of monomer and polymer. Thus, the free volume model allows for the determination of the extent of reaction at vitrification for any temperature between T_{gm} and T_{gp}, since

$$p = \frac{1}{(\rho_m/\rho_p)[(1/\phi_p) - 1] + 1} \tag{4}$$

Using values of ρ_m = 0.90 g/ml, ρ_p = 1.05 g/ml, α_m = 11.7 × 10^{-4}/°C,[7] α_p = 5.5 × 10^{-4}/°C,[7] T_{gp} = 100°C, and T_{gm} = −100°C (assumed), a plot of the predicted values of p at T_g from eq. (4) and eq. (2) is shown in Figure 1. For simplicity ρ_m and ρ_p were taken to be independent of temperature.

A reaction mechanism and the appropriate kinetics are required in order to calculate the time to vitrification. The rate of polymerization of styrene, using a free radical initiator and considering termination by combination only, is[8,9]

$$R_p = -d[M]/dt = k_p[M](fk_d[I]/k_t)^{1/2} \tag{5}$$

where [M] = monomer concentration, f = initiator efficiency, [I] = initiator concentration, and k_p, k_d, k_t = propagation, initiator decomposition, and termination rate constants, respectively. Considering first-order decomposition of the initiator, and from [M] = $[M]_0(1 - p)$, then from eq. (5),

$$-\ln(1 - p) = 2k_p(f[I]_0/k_dk_t)^{1/2}[1 - \exp(-k_dt/2)] \tag{6}$$

where $[M]_0$ = initial monomer concentration and $[I]_0$ = initial initiator concentration. The following model parameters are used:[8]

$[M]_0 = 8.65$ mol/L
$[I]_0 = 0.10$ mol/L
$f = 0.5$
$k_p = (1.62 \times 10^{10}$ L/mol·h$) \exp(-6.21$ kcal mol$^{-1}/RT)$
$k_t = (2.088 \times 10^{11}$ L/mol·h$) \exp(-1.91$ kcal mol$^{-1}/RT)$
k_d (benzoyl peroxide) $= (2.725 \times 10^{17}$ h$^{-1}) \exp(-29.71$ kcal mol$^{-1}/RT)$.

It is assumed that k_p, k_t, and k_d are independent of extent of reaction, i.e., the reactions are not diffusion-controlled until vitrification occurs.

Figure 2 is a plot of reaction temperature vs. time to vitrification, obtained by solving eq. (6) for t, once p is known. The S-shaped vitrification curve is evident, although due to the nature of the kinetic mechanism the vitrification times at low temperatures are physically unrealizable.

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