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Time–temperature transformation of free-volume profile for the curing reaction of unsaturated polyester resin

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The curing reaction of the unsaturated polyester/styrene system was investigated by differential scanning calorimetry (d.s.c.). The variation of the free-volume fraction (V_f) during curing was calculated from d.s.c. data by an empirical equation developed in a previous work, along with Simha and Boyer's free-volume equations. Time–temperature shifts of V_f vs. ln(cure time) data at different curing temperatures showed that there is a critical point 1* after which the free-volume fraction profile formed a master curve with respect to an arbitrary reference temperature and yielded a single Arrhenius activation energy. This result indicated that polymerization after critical point 1* was V_f-dependent only. The experimental data showed that the conversion (α_{cr1^*}) at critical point 1* was higher than gel conversion (α_{cr1}). The gel point (critical point 1) was related to the onset of the overlap of polymer coils. The critical point 1* was related to the onset of the formation of a macro-network without the presence of primary polyester chains, and termination was totally controlled by local segmental diffusion and not by propagating polymer chain self-diffusion. The experimental results also revealed that both α_{cr1} and α_{cr1^*} increased with increasing curing temperature. This behaviour was consistent with Turner's critical concentration model for free-radical polymerization.

(Keywords: unsaturated polyester; free volume; time–temperature shifts)

INTRODUCTION

Unsaturated polyester resin is one of the most important thermosetting resins for preparing sheet and bulk moulding compounds (SMC and BMC), resin transfer moulding (RTM), hand lay-up fibre-reinforced plastics, filament winding fibre-reinforced plastics, etc. Conventional unsaturated polyester is normally prepared by the reaction of a saturated diol with a mixture of an unsaturated dibasic acid and a saturated dibasic acid or their corresponding anhydrides. Commercially, the resin is available in the form of solutions containing 60–70 wt% of a prepolymer dissolved in a reactive solvent (e.g. styrene)[1,2].

The curing reaction between styrene and unsaturated polyester resins is a free-radical polymerization. The reaction of styrene with unsaturated polyester includes not only kinetic reaction but also gelation and network formation. Several researchers[3,4] have reported that, during the early stage of the curing reaction, the long-chain polyester molecules tend to form a spherical-type 'microgel' structure due to intramolecular crosslinking among the pendent C=C bonds of the polyester molecules. In the early stage of curing, the microgels grow in both particle size and number, and start to overlap at a critical conversion, α_{cr1}. After the critical point 1, the termination between the free-radical polymer chains becomes diffusion-controlled, the rate coefficient for termination begins to decrease markedly and the reaction rate increases rapidly. This is the so-called 'gel effect'.

Studies of the gel effect and the kinetics of free-radical polymerization have been reported by several researchers[5–10] and reviewed by Horie *et al.*[11]. The onset of autoacceleration or gel effect in free-radical bulk polymerization was related to the molecular close-packing model of random coils by Turner[5], who examined this experimentally and derived a relationship between the critical polymer concentration C_{cr1} for the onset of gel effect and some average degree of polymerization X of the polymer present in the free-radical polymerization system:

$$C_{cr1}X^{\beta} = K_c(\text{const}) \qquad \text{or} \qquad C_{cr1} \sim X^{-\beta} \tag{1a}$$

Based on an analogy to the change in concentration and molecular-weight dependence of polymer dynamic properties such as viscosity, modulus and compliance when crossing over from a dilute to a more concentrated solution, Turner proposed that the onset of the gel effect corresponds to close packing of macromolecules with unperturbed dimensions ($\beta = 0.5$). The most important and persuasive argument for the onset of the gel effect is the change of diffusion behaviour into the reptation mode in semidilute solution. It was suggested by several authors[6–8] that the overlap concentration C_{olp}, corresponding to the crossover from the dilute to the

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semidilute region, is expressed by equation (2a) according to the scaling theory[9]:

$$C_{\mathrm{olp}} \sim X^{-x} \qquad \text{where} \qquad x = 0.5 \text{ to } 0.8 \tag{2a}$$

During free-radical polymerization, the polymer concentration C is proportional to conversion α, for which equations (1a) and (2a) can be rewritten as:

$$\alpha_{\mathrm{cr1}} X^{\beta} = K_{\mathrm{c}}(\text{const}) \qquad \text{or} \qquad \alpha_{\mathrm{cr1}} \sim X^{-\beta} \tag{1b}$$

$$\alpha_{\mathrm{olp}} \sim X^{-x} \qquad \text{where} \qquad x = 0.5 \text{ to } 0.8 \tag{2b}$$

A kinetic model based on the free-volume theory for free-radical polymerization has been developed by Marten and Hamielec[10]. It has been assumed that the termination reaction becomes diffusion-controlled when the diffusion coefficient for a polymer radical D_{p} becomes less than or equal to a critical diffusion coefficient D_{pcr1}. The diffusion coefficient of a polymer in a solvent can be related to the free-volume fraction and the molecular weight[12]. It has also been assumed that chain entanglements occur soon after the rate constant of termination (k_{t}) becomes diffusion-controlled, according to Marten and Hamielec[10]:

$$k_{\mathrm{t}} = k_{\mathrm{t1}} \left(\frac{M_{\mathrm{wcr1}}}{M_{\mathrm{w}}}\right)^{1.75} \exp\left[-A_1\left(\frac{1}{V_{\mathrm{f}}} - \frac{1}{V_{\mathrm{fcr1}}}\right)\right] \tag{3}$$

$$(\text{for } \alpha_{\mathrm{cr1^*}} > \alpha > \alpha_{\mathrm{cr1}})$$

Here k_{t1} is the termination rate constant for the polymerization at conversion α below critical conversion α_{cr1}; M_{wcr1} is the polymer molecular weight at critical point 1; V_{f} is the free-volume fraction; V_{fcr1} is the free-volume fraction at critical point 1; and A is a constant.

For a crosslinked polymerization system such as unsaturated polyester/styrene, there exists another critical conversion $\alpha_{\mathrm{cr1^*}}$ that is higher than α_{cr1}. At critical point 1*, no primary polyester exists and the polymers are linked as a macro-network. Thus, only the mobility of the local propagating chain is related to the termination. Based on the entanglement idea, k_{t} is inversely proportional to the number of crosslinks per polymer chain[13]. The free volume of the system decreases with the crosslink density. The diffusion coefficient of a local segment is related to the free-volume fraction of the system but not to the polymer molecular weight. Hence, k_{t} can be written as:

$$k_{\mathrm{t}} = k_{\mathrm{t^*}} \exp\left[-A_{1^*}\left(\frac{1}{V_{\mathrm{f}}} - \frac{1}{V_{\mathrm{fcr1^*}}}\right)\right] \tag{4}$$

$$(\text{for crosslinked polymerization with } \alpha > \alpha_{\mathrm{cr1^*}})$$

where $k_{\mathrm{t^*}}$ is the termination rate constant at critical point 1* and $k_{\mathrm{t^*}} < k_{\mathrm{t1}}$.

The diffusion coefficient of a small molecule in a polymer solution can also be related to the free-volume fraction[12]. The fact that the propagation reaction becomes diffusion-controlled at higher conversion means that another critical conversion (α_{cr2}) is reached where the propagation reaction becomes diffusion-controlled. In most cases, the critical point 2 corresponds to the vitrification point at which the cure temperature $T_{\mathrm{cure}} = T_{\mathrm{g}}$. According to Marten and Hamielec[10], the propagation rate constant (k_{p}) beyond α_{cr2} is given by the following expression:

$$k_{\mathrm{p}} = k_{\mathrm{p0}} \exp\left[-B\left(\frac{1}{V_{\mathrm{f}}} - \frac{1}{V_{\mathrm{fcr2}}}\right)\right] \tag{5}$$

$$(\text{for } \alpha > \alpha_{\mathrm{cr2}})$$

where B is a constant, and k_{p0} is the propagation rate constant while conversion α is below α_{cr2}.

If k_{t} and k_{p} given by equations (3) and (5) are inserted into the classic rate expression for polymerization, one obtains[10]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{k_{\mathrm{p0}}^2}{k_{\mathrm{t0}}}\right)^{1/2} \exp\left[-B\left(\frac{1}{V_{\mathrm{f}}} - \frac{1}{V_{\mathrm{fcr2}}}\right)\right] \times \exp\left[\frac{-A_{1^*}}{2}\left(\frac{1}{V_{\mathrm{f}}} - \frac{1}{V_{\mathrm{fcr1^*}}}\right)\right] \times \exp\left[\frac{-A_1}{2}\left(\frac{1}{V_{\mathrm{f}}} - \frac{1}{V_{\mathrm{fcr1}}}\right)\right] (fk_{\mathrm{d}}[\mathrm{I}])^{1/2}(1-\alpha) \tag{6}$$

with characteristic values in four intervals:

Interval 1 ($\alpha < \alpha_{\mathrm{cr1}}$):

$B = 0, A_1 = 0, A_{1^*} = 0, k_{\mathrm{t0}} = k_{\mathrm{t1}}(\text{constant})$

Interval 1* ($\alpha_{\mathrm{cr1}} < \alpha < \alpha_{\mathrm{cr1^*}}$):

$k_{\mathrm{t0}} = k_{\mathrm{t1}}(M_{\mathrm{wcr1}}/M_{\mathrm{w}})^{1.75}, B = 0, A_1 = \text{constant}, A_{1^*} = 0$

Interval 2 ($\alpha_{\mathrm{cr1^*}} < \alpha < \alpha_{\mathrm{cr2}}$):

$k_{\mathrm{t0}} = k_{\mathrm{t^*}} < k_{\mathrm{t1}}, B = 0, A_1 = 0, A_{1^*} = \text{constant}$

Interval 3 ($\alpha_{\mathrm{cr2}} < \alpha$):

$B = 1, A_1 = 0, A_{1^*} = \text{constant}$

Here the critical conversion α_{cr1} is as shown in equations (1b) and (2b), i.e. $\alpha_{\mathrm{cr1}} \sim X^{-\beta}$; and $V_{\mathrm{fcr2}} = 0.025$ (at $T_{\mathrm{cure}} = T_{\mathrm{g}}$); f is the initiator efficiency; k_{d} is the initiator decomposition rate; [I] is the initiator concentration; α is the degree of conversion; and t is the reaction time. For the curing reaction of unsaturated polyester/styrene: critical point 1 corresponds to the point where coils overlap and lead to termination being controlled by both self-diffusion of propagating polymer chains and local segmental diffusion; critical point 1* corresponds to the point for the onset of macro-network formation with termination being controlled only by local segmental diffusion and not by self-diffusion of propagating polymer chains; and critical point 2 corresponds to vitrification (i.e. $T_{\mathrm{cure}} = T_{\mathrm{g}}$) where propagation becomes diffusion-controlled.

In this paper, we show that time–temperature transformation of the free-volume fraction V_{f} vs. $\ln(t_{\mathrm{cure}} - t_{\mathrm{z}})$ (where t_{cure} is the curing time, and t_{z} the induction time for initiator to consume inhibitor) for unsaturated polyester/styrene at different cure temperatures forms a master curve after critical point 1* at an arbitrary reference temperature and yields a single Arrhenius activation energy. The experimental results suggest that the curing reaction after critical point 1* was V_{f}-dependent only. The results also revealed that α_{cr1} and $\alpha_{\mathrm{cr1^*}}$ increase with increasing curing temperature.

This phenomenon is consistent with Turner's critical gel concentration model for free-radical polymerization.

EXPERIMENTAL

Unsaturated polyester

Unsaturated polyester was polymerized from isophthalic acid (IPA), fumaric acid (FA) and propylene glycol (PG) by the usual condensation method. The mole ratio of the final composition of the polyester resin determined by n.m.r. was IPA/FA/PG = 1/1.64/3.23. Thus, the final unsaturated polyester had the following specifications: the acid value was about 28 mg KOH/g, $M_n = 1800$ and $M_w = 4300$.The resin with a styrene/polyester weight ratio of 33/67 and 0.04 wt% of hydroquinone inhibitor was used for the d.s.c. curing study.

Initiator

The peroxide initiator was t-butyl peroxybenzoate from Akzo Chemie Co. with a purity of 98 wt% and an active oxygen content of 8.0 wt%. In this study, 1% by weight of initiator was added to the resin.

Differential scanning calorimetry

A Du Pont 910 DSC was used to measure the exothermic reaction of curing. Hermetic d.s.c. pans were used to minimize losses of volatile materials (such as styrene monomer) during the heating of the sample in the d.s.c. cell. The weight of the sample used ranges from 4 to 6 mg. A small sample was required in order to achieve isothermal operation during cure. In the use of d.s.c. for studying the isothermal curing kinetics of thermosetting resins, one assumes that the amount of heat generated due to the curing reaction is directly proportional to the degree of curing α (or the extent of reaction) of the sample at that time, and then one relates the rate of curing, $d\alpha/dt$, to the rate of heat generated, dQ/dt, by[14]:

$$\frac{d\alpha}{dt} = \frac{1}{Q_{tot}}\frac{dQ}{dt} \tag{7}$$

Integrating equation (7) with time, one obtains the relative degree of cure, α:

$$\alpha = \frac{1}{Q_{tot}}\int_0^t \left(\frac{dQ}{dt}\right)_T dt \tag{8}$$

In equations (7) and (8), the total heat of the curing reaction (Q_{tot}) is given by:

$$Q_{tot} = Q_t + Q_r \tag{9}$$

where Q_t is the heat generated during the isothermal d.s.c. runs, at curing temperature, and Q_r is the residual heat that is released when the sample is heated to 220°C at a heating rate of 5°C min^{-1} after the completion of isothermal curing.

RESULTS AND DISCUSSION

Relation of T_g *with conversion*

For the unsaturated polyester/styrene system, T_g increases as the curing reaction proceeds. Theoretical work on T_g for crosslinked polymers has been reported by several workers[15–17]. Ma *et al.*[18] found that T_g of partially cured unsaturated polyester resins can be related to conversion α by:

$$T_g = K_1 \exp(K_3\alpha) \tag{10}$$

where K_1 and K_3 are constants. Ma *et al.*[18] studied the curing reaction of unsaturated polyester/styrene resins and reported that K_1 and K_3 were 252.0 K and 0.54, respectively, for the same type of resin as that used in the present paper. In the present work, the variation of T_g vs. curing time was calculated from conversion α vs. curing time data obtained from d.s.c. measurements by using equation (10).

Relation of V_f *with* T_g

The variation of the free-volume fraction V_f vs. reaction time was calculated from the data of T_g vs. curing time by using equations (11) and (12)[19]:

$$V_f = V_{fg} + \beta_l(T - T_g) \qquad \text{for } T > T_g \tag{11a}$$

$$V_f = V_{fg} + \beta_g(T - T_g) \qquad \text{for } T < T_g \tag{11b}$$

where $V_{fg} = 0.025$ is the free-volume fraction at T_g, T is the curing temperature, β_l is the thermal expansion coefficient in the liquid state, β_g is the thermal expansion coefficient in the glassy state, and $\Delta\beta = \beta_l - \beta_g$. According to Simha and Boyer, β_l and $\Delta\beta$ have the following relations with T_g for many polymers[20]:

$$\beta_l T_g = 0.164 \tag{12a}$$

$$\Delta\beta T_g = 0.113 \tag{12b}$$

Curing profile

It is known that the curing reaction started only after all of the inhibitor was consumed by the initiator[21]. The time for the initiator to consume the inhibitor is the so-called 'induction time' (i.e. t_z). Since free-radical polymerization proceeds after the induction period, all of the curing profiles in this work were plotted against $(t_{cure} - t_z)$ rather than t_{cure} (where t_{cure} is cure time). *Figure 1* shows conversion α vs. $\ln(t_{cure} - t_z)$ obtained from d.s.c. measurements for unsaturated polyester resin cured at temperatures of 100, 105, 110, 115 and 120°C. The values of t_z for each curing temperature are listed in *Table 1*. The variations of V_f for the same curing resins as

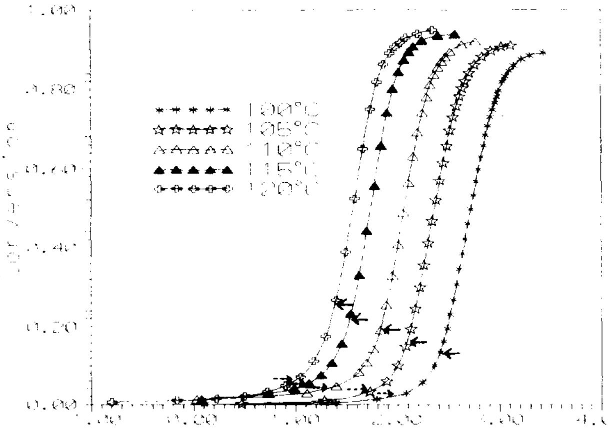
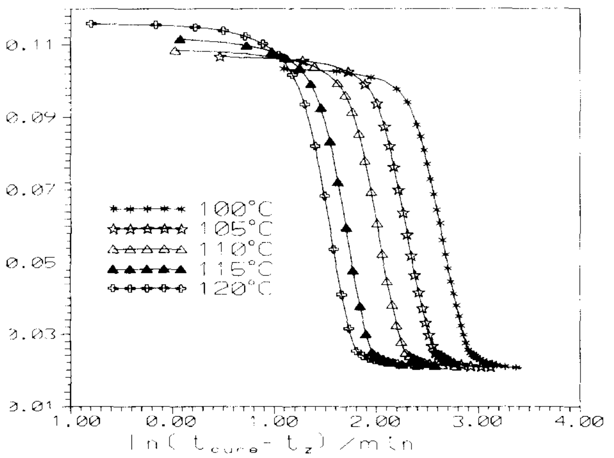


Figure 1 Conversion α vs. $\ln(t_{cure} - t_z)$ for unsaturated polyester/styrene at various curing temperatures obtained from d.s.c. measurement: broken arrow, critical point 1; full arrow, critical point 1*

Table 1 The induction time, shift factor, α_{cr1} and α_{cr1^*}

Cure temperature (°C)	t_z (min)	$A(T)$	α_{cr1}	α_{cr1^*}
100	27.9	reference	0.0323	0.132
105	14.7	0.341	0.0415	0.161
110	7.5	0.618	0.0514	0.185
115	3.0	0.930	0.0577	0.220
120	0.3	1.087	0.0692	0.254



ıre 2 Variations of V_f vs. $\ln(t_{cure} - t_z)$ for unsaturated polyester/styrene at various curing temperatures

shown in *Figure 1* were calculated from equations (10), (11) and (12) and are shown in *Figure 2*.

From equations (3)–(6), we know that the curing reaction for $\alpha > \alpha_{cr1}$ is V_f-dependent after critical point 1 ($\alpha > \alpha_{cr1}$). From equations (3)–(6), we also know that k_{t0} is molecular-weight-dependent for polymerization at a conversion α between α_{cr1} and α_{cr1^*}, and independent of molecular weight after critical point 1* ($\alpha > \alpha_{cr1^*}$). Hence, the variation of V_f after critical point 1* can be described mathematically by the usual kinetic rate equation:

$$\frac{\mathrm{d}\alpha/\mathrm{d}t}{(f[\mathrm{I}])^{1/2}(1-\alpha)} = k(T)F(V_f) \qquad (\text{for } \alpha > \alpha_{cr1^*}) \quad (13)$$

and

$$k(T) = k_{p0}(k_d^{1/2}/k_{t0}^{1/2}) \quad (14)$$

where $k(T)$ is the reaction rate constant, which is a function of temperature, and $F(V_f)$ is some function of the free-volume fraction. At an isothermal curing temperature, the right-hand side of equation (13) is a function of free volume only. Hence, equation (13) can be rewritten as:

$$\frac{\mathrm{d}V_f}{\mathrm{d}t} = k(T)F(V_f)$$

$$(\text{for isothermal curing with } \alpha > \alpha_{cr1^*}) \quad (15)$$

Rearranging equation (15), integrating from t_z to t_{cure} at a constant temperature, and taking the natural logarithm, we get:

$$\ln\left(\int_{V_f(t_{cure}=t_z)}^{V_f(t_{cure})} \frac{\mathrm{d}V_f}{F(V_f)}\right) = \ln k(T) + \ln(t_{cure} - t_z) \quad (16)$$

At $\alpha > \alpha_{cr1^*}$, the left-hand side of the above equation is a function of V_f only. Therefore,

$$F(V_f) = \ln k(T) + \ln(t_{cure} - t_z) \qquad (\text{for } \alpha > \alpha_{cr1^*}) \quad (17)$$

This equation describes the variation of V_f with curing time and temperature. Let V_f vary with time t_{cure1} for curing temperature T_1, and with time t_{cure2} for curing temperature T_2:

$$F(V_f) = \ln k(T_1) + \ln(t_{cure1} - t_{z1}) = \ln k(T_2) + \ln(t_{cure2} - t_{z2}) \quad (18)$$

$$\ln(t_{cure1} - t_{z1}) - \ln(t_{cure2} - t_{z2}) = \ln k(T_2) - \ln k(T_1) \qquad (\text{for } \alpha > \alpha_{cr1^*}) \quad (19)$$

For any two isothermal curing temperatures, $\ln k(T_2) - \ln k(T_1)$ is a constant. When plotted for curing after the critical point 1*, the variation of V_f with curing time at two different curing temperatures (T_1 and T_2) as a function of $\ln(t_{cure} - t_z)$ will have the same functional form except that the curve for the curing temperature T_2 will be displaced from that of the curing temperature T_1 by a constant factor. It follows that if the curing reaction after critical point 1* is only V_f-dependent, all V_f vs. $\ln(t_{cure} - t_z)$ curves at different curing temperatures should be superimposable, by simply shifting each curve along the $\ln(t_{cure} - t_z)$ axis relative to a curve at an arbitrary reference temperature, using a shift factor, $A(T) = [\ln(t_{cure} - t_z)_{ref} - \ln(t_{cure} - t_z)_T]$, for each temperature relative to the reference temperature. The V_f vs. $\ln(t_{cure} - t_z)$ curves of the unsaturated polyester/styrene system cured at various temperatures are shifted along the $\ln(t_{cure} - t_z)$ axis and shown in *Figure 3*. The portion of each curve for $\alpha > \alpha_{cr1^*}$ coincides with that of the curve at $T_{ref} = 100$°C and they form a master curve at 100°C. The shift factors, $A(T)$, used in shifting the curves relative to $T_{cure} = 100$°C are summarized in *Table 1*.

It can be seen from *Figure 3* that V_f data after the critical point 1* for all curing temperatures can be superimposed to form a master curve. The V_f at the critical point 1* was around 0.084 and branched off from the master curve for $\alpha < \alpha_{cr1^*}$ as designated by an arrow in *Figure 3*. The conversions corresponding to $V_f = 0.084$

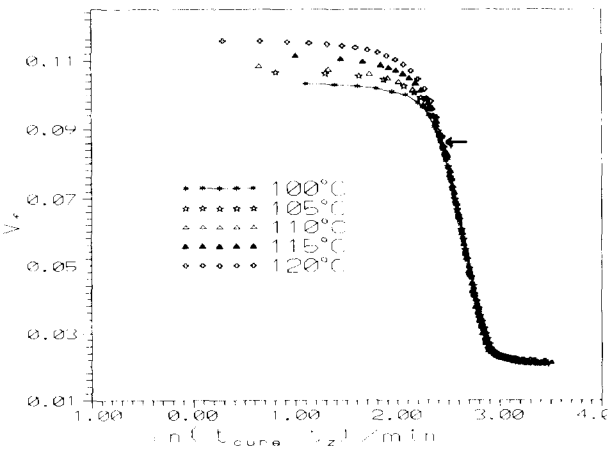


Figure 3 Superposition of the V_f vs. $\ln(t_{cure} - t_z)$ at 100°C with constant shift factor $A(T)$ for each conversion

(i.e. $\alpha_{\mathrm{cr}1^*}$) at different curing temperatures are designated in *Figure 1* by arrows. The values of $\alpha_{\mathrm{cr}1^*}$ for various curing temperatures are also shown in *Table 1*. It is known that the gel effect of unsaturated polyester/styrene begins at the onset of polymerization[22]. In the present work, we define the inflection of the curing rate, $d\alpha/dt$, vs. curing time curve (where curing rate begins to rise rapidly) as the gel point (critical point 1). The critical point 1 at various curing temperatures is also indicated by dashed arrows in *Figure 1* and the values of $\alpha_{\mathrm{cr}1}$ are also summarized in *Table 1*. The critical point 1 is related to the onset of overlap of polymer coils where physical entanglement of polymer chains occurs. The critical point 1* is related to the point where no primary polyester chain exists and the polymer chains are linked through chemical reaction to form a macro-network with residual reactive vinyl groups within the network. After critical point 1* termination is controlled only by local segmental diffusion. Between critical point 1 and critical point 1*, termination is controlled by both self-diffusion of the propagating polymer chains and local segmental diffusion. Thus both polymer molecular weight and free volume are related to termination before critical point 1*. However, after critical point 1* only free volume is related to termination. Because of the influence of the kinetically controlled termination reaction (for $\alpha < \alpha_{\mathrm{cr}1}$) along with polymer molecular-weight dependence (for $\alpha < \alpha_{\mathrm{cr}1^*}$), V_f data for curing temperatures higher than 100°C branched off from the master curve before critical point 1*.

For a steady-state free-radical polymerization, the temperature dependence of the rate constant is generally given by an Arrhenius relationship[21]:

$$k(T) = A_0 \exp\left(\frac{-E}{RT}\right) = \frac{A_{\mathrm{d}}^{1/2} A_{\mathrm{p}}}{A_{\mathrm{t0}}^{1/2}} \exp\left(\frac{(E_{\mathrm{d}} + 2E_{\mathrm{p}} - E_{\mathrm{t}})/2}{RT}\right) \qquad (20)$$

where E is the activation energy, R the gas constant and A_0 an Arrhenius constant. The shift factors listed in *Table 1* can be used to calculate the Arrhenius activation energy for the polymerization, since equation (19) provides the relationship between the time shift factors and the rate constants:

$$A(T) = \ln(t_{\mathrm{cure}} - t_z)_{\mathrm{ref}} - \ln(t_{\mathrm{cure}} - t_z)_T = \ln k(T) - \ln k(T_{\mathrm{ref}}) = -\frac{E}{RT} + \frac{E}{RT_{\mathrm{ref}}} \qquad (21)$$

When T_{ref} is fixed and all other data are shifted relative to the reference temperature (for the present case $T_{\mathrm{ref}} = 100°\mathrm{C}$), plotting the shift factor $[\ln(t - t_z)_{\mathrm{ref}} - \ln(t - t_z)_T]$ against $1/T$ should yield a straight line with slope given by $-E/R$ and intercept E/RT_{ref}. The shift factors in *Table 1* are plotted against $1/T$ and shown in *Figure 4*. The resulting plot is a straight line, the slope of which yields an activation energy of 67.6 kJ mol^{-1}. The value of the activation energy was consistent with that of typical free-radical polymerization. (The values of E_{p}, E_{t} and E_{d} for free-radical polymerization of styrene with peroxybenzoate initiator are 26, 8.0 and 134 kJ mol^{-1} respectively[21]. Thus, the activation energy for the polymerization of styrene is $E = E_{\mathrm{d}}/2 + E_{\mathrm{p}} - E_{\mathrm{t}}/2 =$ 89 kJ mol^{-1}). These results suggest that after critical point 1* there is only one V_f-dependent reaction mechanism with a single overall apparent activation energy.

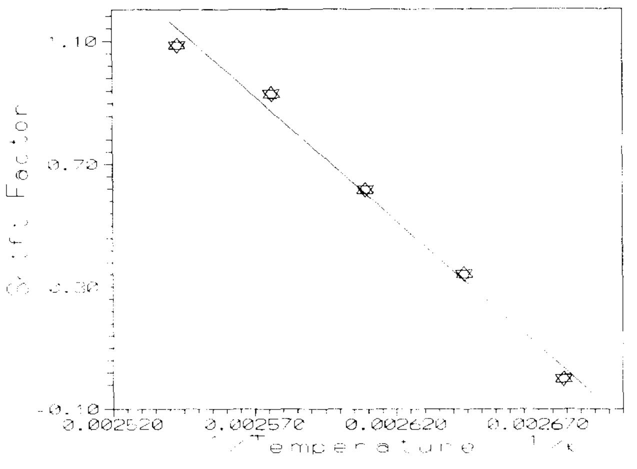


Figure 4 Arrhenius plot of the shift factors $A(T)$ vs $1/T$

From *Table 1*, it is obvious that both $\alpha_{\mathrm{cr}1}$ and $\alpha_{\mathrm{cr}1^*}$ increase as the curing temperature increases. It is known that for a biomolecular termination free-radical polymerization, the degree of polymerization X_n is given by[21]:

$$\ln X_n = \ln\left(\frac{A_{\mathrm{p}}}{(A_{\mathrm{d}} A_{\mathrm{t}})^{1/2}}\right) + \ln\left(\frac{[\mathrm{M}]}{(f[\mathrm{I}])^{1/2}}\right) - \frac{E_{X_n}}{RT} \qquad (22)$$

where A_{d}, A_{p} and A_{t} are the Arrhenius constants for the rate constants of initiator dissociation, free-radical propagation and free-radical termination respectively; f is the efficiency of the initiator; [I] is the initiator concentration; [M] is the vinyl group concentration; and E_{X_n} is the activation energy. The activation energy E_{X_n} for typical thermally initiated free-radical polymerization is around -45 kJ mol^{-1} (ref. 21). Equation (22) indicates that before the critical point 1 the polymer chain length of the unsaturated polyester/styrene system decreases as the curing temperature increases. According to Turner's critical concentration model[5] for free-radical polymerization (i.e. equations (1) and (2)), $\alpha_{\mathrm{cr}1}$ decreases as the polymer chain length increases. Thus the increase in curing temperature resulted in a higher $\alpha_{\mathrm{cr}1}$. In his paper, Turner[5] summarized the experimental results of previous work[23–26] for the free-radical polymerization of methyl methacrylate and indicated that $\alpha_{\mathrm{cr}1}$ increased as the temperature of free-radical polymerization increased. The behaviour of the free-radical polymerization of methyl methacrylate is consistent with the present work.

CONCLUSIONS

Time–temperature shifts of V_f vs. $\ln(t_{\mathrm{cure}} - t_z)$ data for the unsaturated polyester/styrene system at different cure temperatures formed a master curve after critical point 1* at an arbitrary temperature and yielded a single Arrhenius activation energy. The results revealed that progress of polymerization after critical point 1* was a function of free volume. The experimental data also indicated that the critical conversion $\alpha_{\mathrm{cr}1}$ and $\alpha_{\mathrm{cr}1^*}$ increased as the curing temperature increased. This result is consistent with Turner's critical concentration model for free-radical polymerization.

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