Effect of diffusion control in the glass transition region on critical conversion at the gel point during curing of epoxy resins

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An investigation into curing of Bisphenol A diglycidyl ether with an amine curing agent was carried out both above and below the glass transition temperature, T_g, of the reacting system. At T_g curing was still partly controlled by chemical kinetics. The critical gel point conversion was the same, irrespective of whether curing occurred above or below T_g. Such independence indicated that all reaction steps were retarded to the same degree when viscosity increased.

INTRODUCTION

Formation of macromolecular compounds and polymer networks may be accompanied by a considerable rise in the glass transition temperature, T_g, of the reacting system. In such a case, at constant reaction temperature, the reacting system passes through the main transition region, segmental motions are slowed down and the chemical reaction is controlled rather by these motions than by chemical factors. If T_g becomes sufficiently higher than the reaction temperature, the reaction practically ceases to proceed. The extent of segmental motion depends on the difference between the reaction temperature and T_g and is expressed in terms of the Williams–Landel–Ferry (WLF) superposition principle; it has been found that this theory adequately describes time changes of the glass transition temperature T_g in the crosslinking of polyester resins[1,2].

The curing of epoxy resins is an example of a crosslinking reaction in which T_g of the reacting system frequently becomes higher than the reaction temperature T, and the curing ceases, owing to diffusion control before all functional groups have reacted (see, for example, refs 3–5). It is not clear whether the mobility and thus also the apparent reactivity of all functional groups decrease to the same extent, or whether they depend on the size of the molecule to which the group is attached. A sensitive indication of the course of the crosslinking reaction is the critical conversion of functional groups at the gel point. If reactions of groups attached to smaller rather than to larger particles were preferred, the degree of polymerization distribution would become narrower and the critical conversion would be shifted to higher values with the decreasing difference, $\theta = T - T_g$. Such diffusion control could also have practical consequences, because the network formed could have a different structure, even if the same resulting conversion were reached.

In our earlier papers we investigated network formation in the curing of Bisphenol A diglycidyl ether (BADGE) with various diamines[6,7] up to and beyond the gel point under conditions when the reacting system was in the liquid or rubbery state. Analysis of the curing and model reactions, leading only to low molecular weight compounds[8], showed that the curing was controlled merely by the chemical reactivity of groups. The network formation depended only on the starting molar ratio of functional groups, on conversion and on the reactivity ratios for hydrogen atoms on the primary and secondary amino groups.

In this work we have investigated the effect of diffusion control on the gel point conversion in the curing of BADGE with 4,4′-diamino-3,3′-dimethyldicyclohexylmethane.

EXPERIMENTAL

BADGE used previously[7] was cured with 4,4′-diamino-3,3′-dimethyldicyclohexylmethane (Laromin 260, BASF GFR, used as received) at 40°–130°C in Teflon moulds. At the same time, the dependence of T_g on the conversion of functional groups was determined by the d.s.c. method (Perkin–Elmer DSC-2, using a heating rate of 10°C/min for each sample in order to prevent a shift of the conversion during the measurement). The conversion of the epoxy groups was determined by titration and the gel point from solubility[7]. At 130°C the ratio, r, of the rate constants for hydrogen atoms on the primary and secondary groups was determined ($r = 0.25–0.35$), using the method of critical stoichiometric ratio[6,7]. At 130°C, θ varied during the reaction from 150 to 50K. The critical conversion was calculated (*Table 1*) for the molar ratio of amine hydrogen atoms to epoxy groups $E_a = 2$, and $r = 0.30$.

RESULTS AND DISCUSSION

Comparison of experimental results obtained for curing temperatures 100°, 64° and 40°C clearly showed that at 64° and 40°C curing was considerably slowed down or even ceased because of the diffusion control.

The diffusion control can be clearly seen from the time

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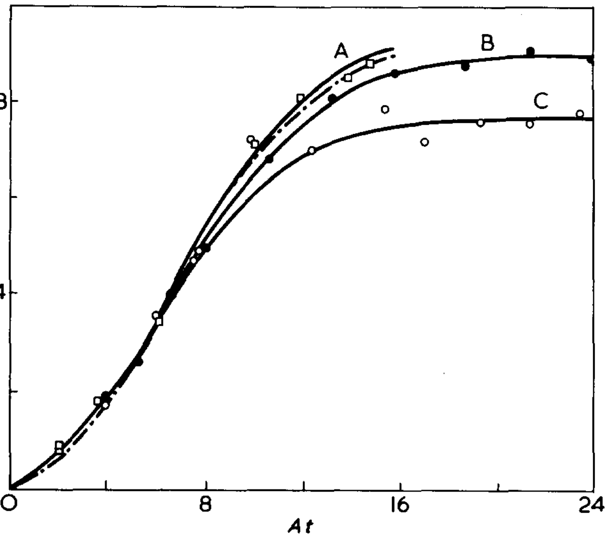

Figure 1 Time dependence of conversion of epoxy groups in the reaction of 4,4'-diamino-3,3'-dimethyldicyclohexylmethane with bisphenol A diglycidyl ether ($a_0/b_0 = 2$). Initial course is superimposed by the multiplicative factor A. Reaction temperature (°C): A, 100, $A = 1$; B, 64, $A = 0.133$; C, 40, $A = 0.0308$; — · — · —, calculated from the integrated equation (2) (see text), $c_0 = 0.03$

dependences of the conversion of the epoxy groups, ξ, the beginnings of which may be superimposed by a multiplicative factor A on the time scale (*Figure 1*). After reaching $\theta \approx -25$K, any further increase in ξ cannot be measured. T_g increases during curing (*Figure 2*) and, at a given E_a, T_g is a function only of conversion and not of the curing temperature. *Figure 2* also shows the proximity of the systems to T_g. At 40°C, the reaction ceased before the gel point at $\xi = 0.75$–0.80, and therefore the temperature was subsequently raised to 64°C (*Figure 2*). The experimentally determined T_g is somewhat higher than the real one because of the fast heating in d.s.c. measurements. This increase in T_g is estimated as 5°–6°C which follows from the dependence of T_g on the rate of heating for a system prepared at the critical stoichiometric ratio and with fully reacted epoxy groups. For instance, T_g increased by 2.5°C when the rate of heating increased from 1.25° to 10°C/min.

It is clear that the reaction is stopped by diffusion control, but it is of interest to find out whether the diffusion control is already fully operative near T_g. The transition from chemically to diffusion controlled reactions can be analysed from the temperature dependence of the rate constant k_T: in the region of chemical control $\log k_T \sim 1/T$, while in the region of the viscoelastic diffusion control $\log k_T/k_{T_g}$ is proportional to $\theta/(\theta + c_2^g)$ or $1/(\theta + c_2^g)$ (ref 2), determined from the free volume theory and expressed in terms of the WLF equation[9]. In our case we did not determine the rate constants: instead, we employed the reaction rate $d\xi/dt$ which may be separated[10] into the temperature-dependent k_T and the temperature-independent $F(\xi,r)$ terms:

$$\xi' \equiv d\xi/dt = k_T F(\xi,r) \qquad (1)$$

For an autocatalysed reaction, the activation energies of the reaction, both uncatalysed and catalysed with forming OH groups, are virtually the same[3]. $F(\xi,r)$ can therefore be written as:

$$F(\xi,r) = (1 - \xi)(\xi + c_0)(a_p + r a_s) \qquad (2)$$

where r is the ratio of the rate constants $k_2/2k_1$, a_p and a_s are concentrations of the primary and secondary amino groups and c_0 corresponds to the initial reaction rate. For a given r and E_a, a_p and a_s can be calculated from ξ[3,6–8]. Hence, the term $F(\xi,r)$ expresses a change in the rate given by a change in the concentration of functional groups and is very little temperature-dependent (r varies with temperature very little)[3]. In chemically controlled reactions $F(\xi,r)$ determines the shape of the conversion curve, since

$$\int_0^{\xi} [1/F(\xi,r)] d\xi = k_T t$$

and *Figure 1* shows that the shapes of the calculated and kinetic curves at 100°C differ very little. For a purely diffusion controlled reaction k_{T_g} ought to be constant. However, ξ'_{T_g} values obtained by extrapolation or interpolation at constant conversion increase distinctly, and the difference amounts to 1.4–1.5 of the logarithmic decade if T_g increases from 0° to 80°C. At the same time, the function $F(\xi,r)$ beyond the inflexion point has a decreasing trend with increasing ξ, and consequently so has T_g; after correction for the conversion dependence the above difference would increase by 1.8 of the logarithmic decade. This suggests that at T_g the reaction is still partly chemically controlled, and that the assumption of a constant k_{T_g} (ref 2) should be taken with reserve. The fact that the diffusion control has already become partly operative at T_g is indicated by a decrease in the apparent activation energy of reaction

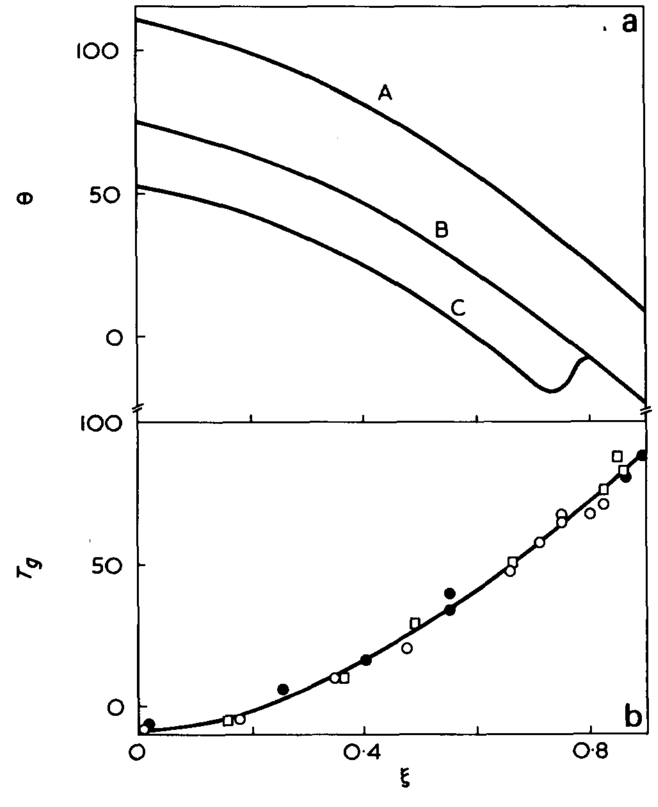

Figure 2 Dependence of the glass transition temperature T_g and of the difference θ between the reaction temperature and T_g, $\theta = T - T_g$, on conversion of epoxy groups. Reaction temperature T(°C): A, □, 100; B, ●, 64; C, ○, 40 (64)

Table 1 Dependence of critical conversion at the gel point in the curing of BADGE with 4,4′-diamino-3,3′-dimethylcyclohexylmethane at various temperature

T(°C)	ξ_c
130	0.89
100	0.87
64	0.89
40(64)	0.89

from ~ 14 kcal/mol[3] (low conversion and high $T - T_g$) to 9–10 kcal/mol ($T = T_g$) obtained from the temperature dependence of k_{T_g}. These conclusions still hold qualitatively, even if T_g values are reduced by 10K. This is clearly the main reason for the curvature of WLF plots near T_g; another reason may be a change in the WLF constants with conversion, because macromolecular compounds are gradually formed in the system from the low molecular weight ones.

Regardless of the extent of diffusion control on the curing reaction, the critical conversion at the gel point is virtually constant (*Table 1*). In other words, the decrease in the reaction rate caused by the decrease in segmental mobility in the main transition region affects all functional groups to the same extent irrespective of the size of particles to which these groups are attached. The viscosity of the system is clearly the only decisive factor.

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