Etherification reaction in epoxy–amine systems at high temperature

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Most kinetic studies of epoxy–amine systems have focused on the rate of reaction between epoxy and amino groups. The etherification reaction, which occurs at higher temperature and later stages of cure, has been addressed by few investigators. An expression for the rate of etherification in a model compound system, composed of phenyl glycidyl ether(1,2-epoxy-3-phenoxypropane) and aniline is presented in this paper.

(Keywords: cure; crosslinking; epoxy)

Introduction

Since Castan's seminal work[1], over half a century ago, epoxy resins have graduated from a laboratory curiosity to a multitude of applications in the adhesive, electronic and aerospace industries. Depending on the intended use, one can nowadays choose between numerous epoxy formulations with a wide variety of compositions and properties.

Over the years, the mechanism and kinetics of epoxy–amine reactions have generated considerable interest, and several key reviews of the subject have been published[2–6]. But despite the wealth of published information, the subject of epoxy–amine cure continues to attract researchers in their efforts to resolve contradictory findings and answer unresolved questions.

We have recently reported the results of our comprehensive study of epoxy–amine reactions using model compounds and multifunctional formulations[7–9]. We investigated the substitution effect and the reactivity ratio as a function of chemical composition, temperature and degree of cure, and put forward a mechanistic reaction model based on the existence of different transition complexes.

In this communication we report the results of our recent study of the kinetics of etherification, which is known to occur in epoxy–amine systems at high temperatures and at late stages of reaction, or in the presence of a large excess of epoxy groups[10–14].

The primary objective of this study was to determine the kinetic parameters for etherification in a model system and compare them with the corresponding values for the primary amine–epoxy and secondary amine–epoxy reactions.

Experimental

Materials. The model compound formulation consisted of 1,2-epoxy-3-phenoxypropane (also known as phenyl glycidyl ether, PGE; 99%, Aldrich) and diamino diphenylsulfone (DDS, Aldrich).

Technique. High performance liquid chromatography (h.p.l.c.) was used to calculate the concentrations of different species in the reaction mixture. C18 reversed phase column was used to separate the mixture into its components. Gradient elution of methanol–water mobile phase at a flow rate of 1.75 ml min^{-1} was utilized. Further details of our experimental procedure are available elsewhere[9].

Results and discussion

Every epoxy–amine reaction produces a hydroxyl group, which may react with another epoxy to produce ether. That reaction, referred to as etherification, generally occurs in epoxy-rich systems, at higher temperature and in the later stages of reaction. The model compound system (PGE–DDS) was selected because of its relatively high reaction temperature—the condition which favours etherification.

The effect of stoichiometry was studied first. *Figure 1* shows h.p.l.c. chromatographs of the reaction products found in four PGE–DDS systems with varying amine/epoxy ratios. All systems were cured isothermally at 160°C for 46 h. Consecutive reactions occur in PGE–DDS systems, as shown in *Scheme 1*, and h.p.l.c. assignments are made to identify various products in the order of their appearance in chromatograms. The ether peaks are those eluted after 23.55 min (*Figure 1*). Judged by the increase in the magnitude of ether peaks relative to an unchanged component, etherification appears negligible in the stoichiometric system but gradually becomes more pronounced at higher epoxy/amine ratios.

A quantitative kinetic analysis of etherification was conducted next. We selected a PGE–DDS mixture with excess epoxy (epoxy/amine ratio = 1.6) and investigated isothermal reactions at 160, 170 and 180°C. The choice of high temperature and excess epoxy was intended to promote etherification in the hope that a noticeable change in the concentration of reactants would be observed. To simplify the analysis, reactions between epoxy and amino groups were eliminated from consideration. That was made possible by carrying out the analysis on systems in which all reactive amino hydrogens have been consumed, corresponding to a complete

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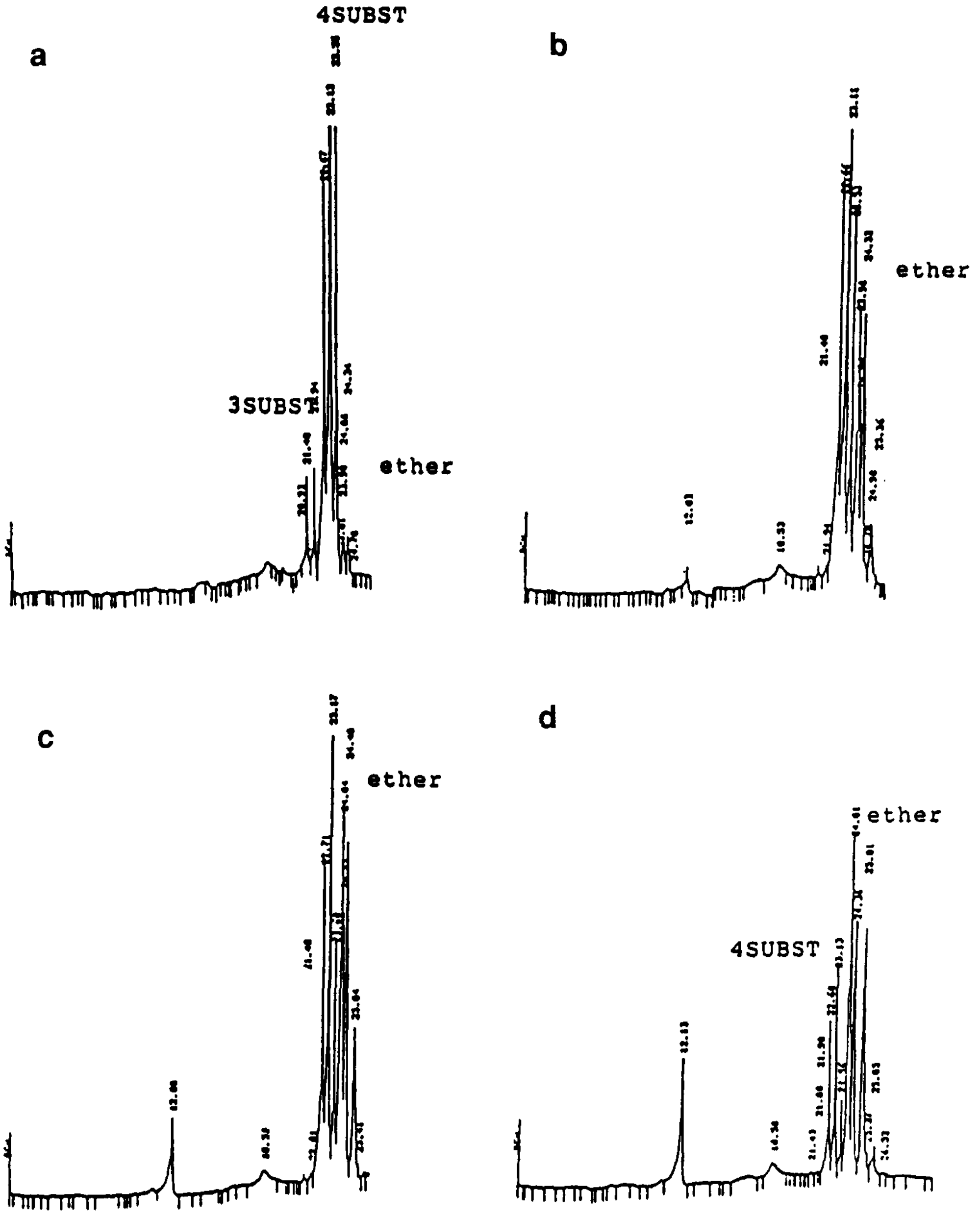


Figure 1 H.p.l.c. chromatographs of four PGE–DDS systems with different compositions (mol PGE/mol DDS): (a) 1.0; (b) 1.2; (c) 1.4; (d) 1.8. All systems were reacted at 160°C for 46 h

conversion of 3SUBST into 4SUBST (*Scheme 1*). It is assumed that beyond that point the consumption of 4SUBST occurs solely due to the etherification reaction between epoxy and hydroxyl groups of the 4SUBST. The overall rate of etherification was studied but no attempts were made to elucidate the molecular mechanism.

In the course of etherification, a new hydroxyl group is generated for every one consumed and hence the concentration of hydroxyl groups remains constant. Once all amino groups have been consumed, the rate of etherification becomes independent of hydroxyl concentration and the rate constant for etherification can be obtained from the following kinetic scheme:

$$\mathrm{PGE} + \mathrm{4SUBST} \xrightarrow{k_e} \text{etherified 4SUBST} \qquad (1)$$

$$\mathrm{d[4SUBST]}/\mathrm{d}t = -k_e\mathrm{[4SUBST][PGE]} \qquad (2)$$

where PGE and 4SUBST are as defined in *Scheme 1*.

The concentration profiles of PGE and 4SUBST as a function of time at three different temperatures are shown in *Figure 2*. The observed change in the concentration of 4SUBST during reaction is small. The rate of consumption of 4SUBST was calculated from the experimental results using the following integrated form of equation (2):

$$k_e = -\frac{\mathrm{[4SUBST]}/_{t=t_2} - \mathrm{[4SUBST]}/_{t=t_1}}{\int_{t_1}^{t_2}\mathrm{[4SUBST][PGE]}\,\mathrm{d}t} \qquad (3)$$

The calculated rate constants are plotted as a function of temperature in the Arrhenius form in *Figure 3*. At 160 and 170°C, the etherification rate constant, k_e, was calculated to be equal to $0.000281\,\mathrm{l\,mol^{-1}\,min^{-1}}$ and $0.000311\,\mathrm{l\,mol^{-1}\,min^{-1}}$, respectively. Compared with the value of reaction rate constant for non-catalysed primary amine–epoxy reaction at the same temperature[9], which is on the order of $(3\text{–}5)\times10^{-3}\,\mathrm{l\,mol^{-1}\,min^{-1}}$, the etherification reaction is about 10–15 times slower. This finding

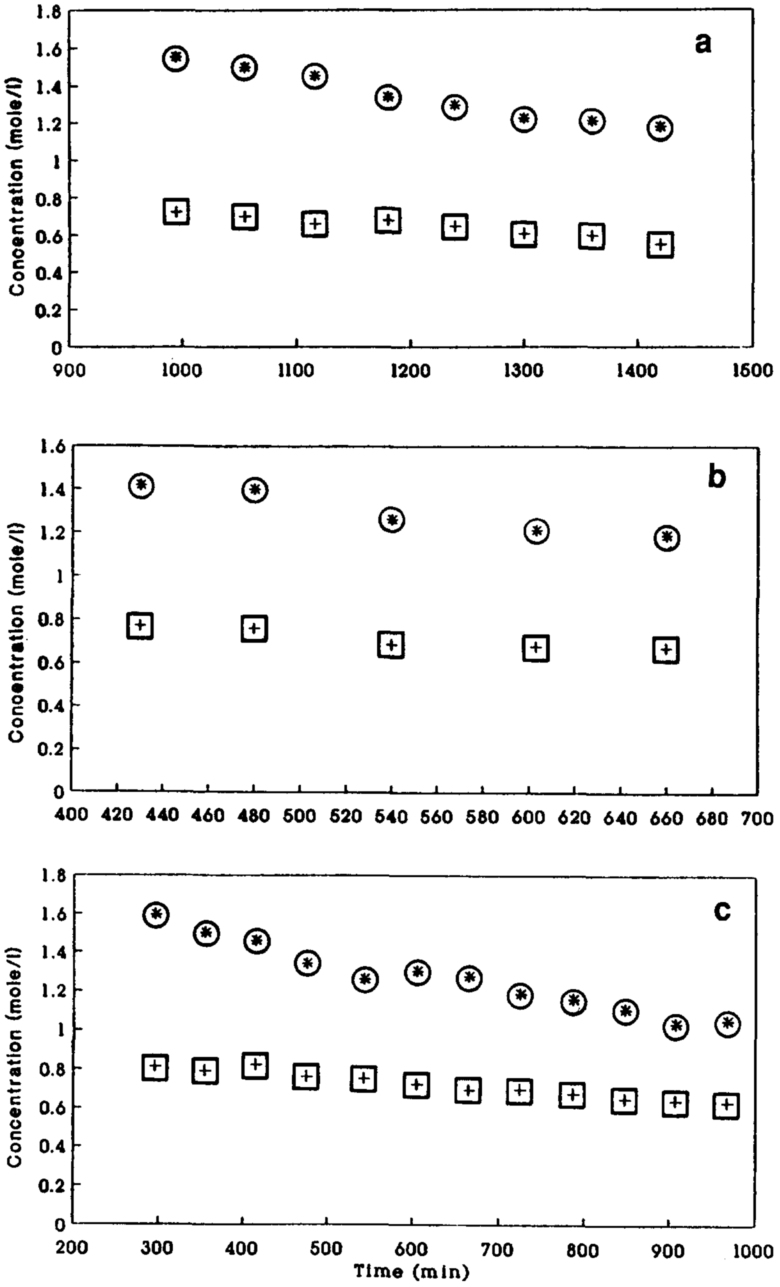


Figure 2 Concentration profiles of PGE (○) and 4SUBST (□) as a function of time in the PGE–DDS system (amine/epoxy ratio = 1.6) at: (a) 160°C; (b) 170°C; (c) 180°C

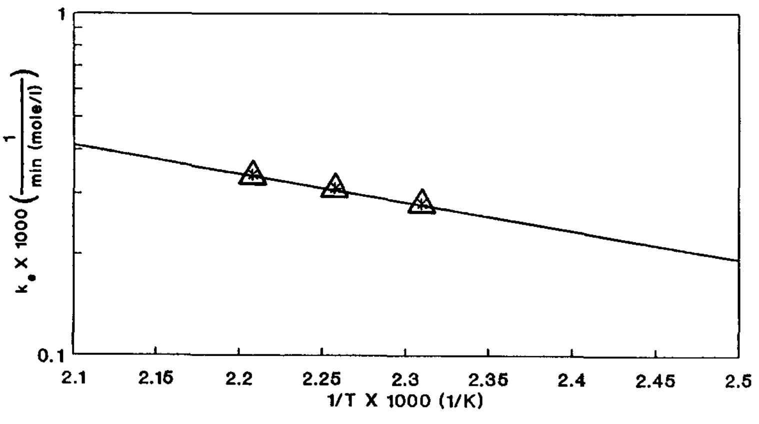
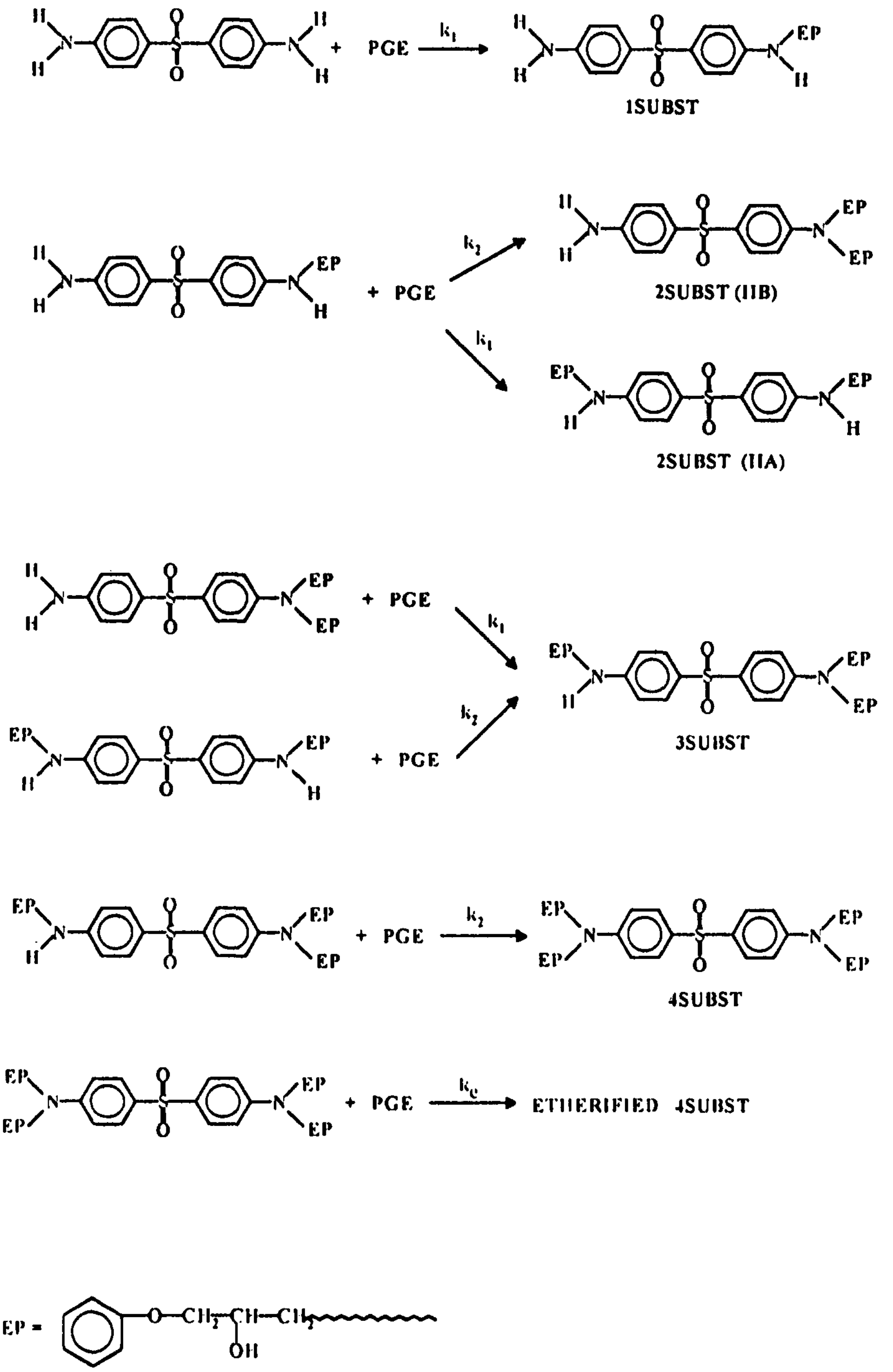


Figure 3 The Arrhenius plot for etherification rate in the PGE–DDS system



Scheme 1 Consecutive reactions in a PGE–DDS model compound

is in excellent agreement with earlier reports by Morgan and Mones[14].

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