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## DIGLYCIDYL AMINE-EPOXY RESIN NETWORKS: KINETICS AND MECHANISMS OF CURE

N. A. ST JOHN\* and G. A. GEORGE†‡

\*Department of Chemistry, University of Queensland 4072, Australia

†School of Chemistry, Queensland University of Technology, Brisbane, Australia

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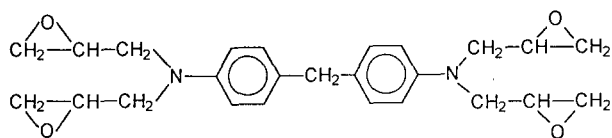
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### 1. INTRODUCTION

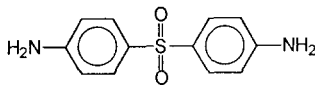
Amine cured epoxy resins produce highly crosslinked glassy matrices with good chemical resistance and adhesive properties.<sup>1</sup> Many graphite-fiber-reinforced composite materials are based on the epoxy resin *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM – 1) with the hardener 4,4'-diaminodiphenylsulphone (DDS – 2).<sup>2</sup> The high epoxy functionality of TGDDM and phenyl structural units result, after cure, in materials with high glass transition temperatures ( $T_g$ ) of 230–280°C.<sup>2</sup> Other glycidyl amine-based functional resins have been synthesized with a lower potential crosslink density through a larger aromatic skeleton<sup>3,4</sup> but the TGDDM structure has had the widest acceptance and several different commercial versions of this resin are available.<sup>5</sup>

The use of TGDDM in aerospace composite materials has ensured that the cure kinetics and mechanisms of this resin, particularly with aromatic amines in the presence or absence of Lewis acids and related catalysts, have been widely studied over a range of temperatures.<sup>6,7,8</sup> In the fabrication of composites, the transformation

‡To whom correspondence should be addressed.



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of the liquid resin to a rubber at the gel point and then to a glass is a critical process and ultimately depends on the chemical kinetics of the system. Time-temperature-transformation diagrams provide an empirical approach for the establishment of a cure cycle for an epoxy resin-hardener system at any particular temperature.<sup>9</sup> However, the development of a predictive model which may ultimately be used to control the processing of the epoxy resin composite requires detailed chemical kinetic data. An example of this approach is the analytical model of Springer *et al.* in which empirical kinetic analysis of a curing epoxy resin is used to predict and control the full cure cycle of the composite material.<sup>10</sup> Any further refinement of this approach requires a more reliable analysis of the curing kinetics and a deeper understanding of the mechanism of the crosslinking reactions which lead to network formation. This has proven possible through the application of instrumental analysis techniques such as NMR and FT-IR spectroscopy<sup>7</sup> to complement traditional DSC methods,<sup>8</sup> as well as detailed studies of model compounds as facilitated by HPLC combined with the above spectroscopic techniques. These have brought to light a rich complexity in the reactions which may occur, as well as an understanding of the often subtle catalytic effects which trace amounts of unavoidable impurities in the resins will produce. This is now allowing an understanding of the variability in the cure and properties of composite materials when fabricated under apparently identical conditions.

In this review, recent studies on the cure kinetics of glycidyl amine epoxy resins will be considered initially from information available based on model systems. The limitations of this approach when extended to the multifunctional resin, with its attendant reaction complexity, will also be considered. The role of modern analytical methods will be emphasized throughout this review.

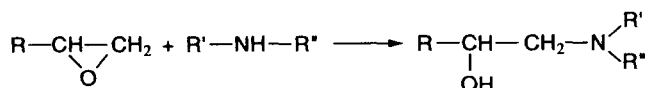
## 2. EPOXY-AMINE CURE CHEMISTRY BASED ON MODEL STUDIES

The oxirane functional group, commonly referred to as an epoxy group, has an enhanced reactivity compared to other cyclic ethers owing primarily to ring strain. This higher reactivity has made epoxy compounds very useful in synthetic chemistry. The reaction of epoxy groups with amines and alcohols is characterized by the three reactions shown as Schemes 1-3.

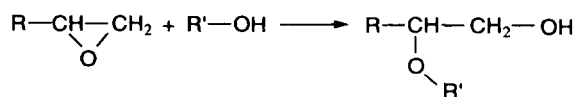
However, in the reaction of epoxides with amines, it has been found that the acidity of amines is generally insufficient for any reaction to proceed without the presence of some form of catalyst. Holubka *et al.*<sup>11</sup> have performed molecular orbital calculations for the reaction of ethylene oxide and ammonia involving no catalysis and catalysis by a hydrogen ion or water. The derived reaction energetics showed a significant catalytic



SCHEME 1. Primary amine-epoxy addition.



SCHEME 2. Secondary amine-epoxy addition.

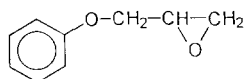


SCHEME 3. Hydroxyl-epoxy addition (etherification).

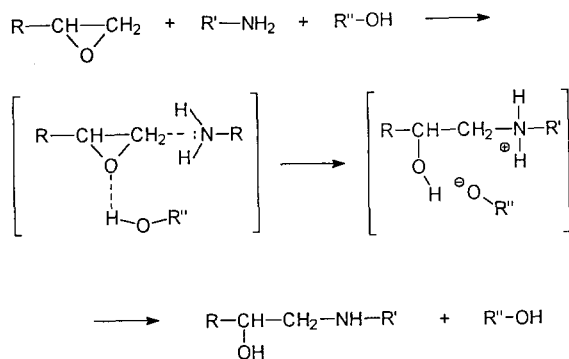
effect by water, as well as hydrogen ions, on the rate of oxirane cleavage, and clearly showed the positive mechanistic effect of additives such as proton donors upon the rate of epoxide reaction.

### 2.1. Glycidyl ether model studies

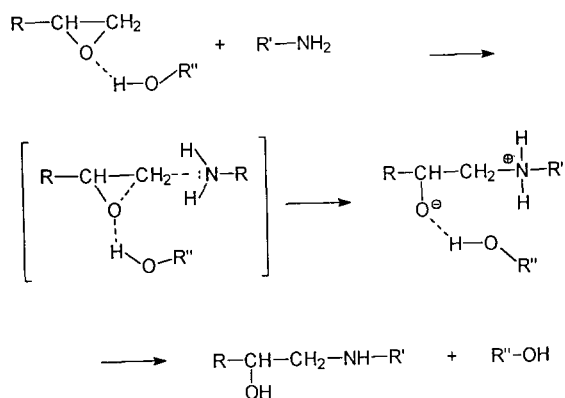
Shechter *et al.*<sup>12,13</sup> studied the reaction of phenylglycidyl ether (PGE), compound **3**, with various simple amines and observed a marked autocatalytic effect by the hydroxyl groups produced in the epoxy-amine addition reaction (Scheme 1). There was negligible reaction between epoxy and hydroxyl groups, however (Scheme 3). They also studied the influence of various solvents and found that compounds with hydroxyl groups or groups that increased the hydrogen ion activity (e.g. nitromethane) had a significant catalytic effect on the epoxy-amine reaction, while other polar solvents such as acetone and benzene actually had a retarding effect. To explain the specificity of hydroxyl groups in accelerating epoxy-amine reactions, a termolecular transition complex was suggested, as shown in Scheme 4.

**3**

Smith<sup>14</sup> analysed the results of Shechter *et al.*, and other workers, and considered that the formation of a termolecular complex was less likely than a two-body collision. He proposed the presence of a preformed hydrogen-bonded complex between epoxy and hydroxyl groups which would then react with an amine, as shown in Scheme 5, to form a transition state similar to that for the termolecular mechanism of Shechter. Smith noted that in the absence of a solvent capable of hydrogen bonding autocatalysis by the hydroxyl groups produced in the reaction was observed. However, when sufficient solvent is present, the solvent may act as an inhibitor of autocatalysis by hydrogen bonding with the hydroxyl groups produced.

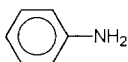


SCHEME 4.



SCHEME 5.

Rozenberg has studied the reaction of epoxy oligomers with amines in detail<sup>15</sup> and addressed the question of whether there exists a 'non-catalyzed' reaction mechanism for epoxy-amine reaction. By obtaining PGE and aniline (**4**) in a very pure form, free from impurity hydroxyl groups and moisture, it was found that the initial reaction rate was proportional to the square of the aniline concentration. This suggested that aniline is not only the nucleophilic reagent but is also capable of acting as an electrophile that catalyzes the reaction. A mechanism similar to Scheme 5 can thus be proposed with a primary amine group replacing the hydroxyl group in the preformed complex as shown in Scheme 6.

**4**

It is clear that hydrogen-bonded complexes are of paramount importance when considering the reaction of epoxide. Rozenberg<sup>15</sup> discussed the significance of such donor-acceptor complexes to the thermodynamics of epoxy amine reactions. He also acknowledged that at the time detailed kinetic data necessary to determine the contributions of such complexes were unavailable, even for low molecular weight systems.

Figure 1 shows some of the donor-acceptor complexes that can form in a typical epoxy-amine system. The complexes can be considered in terms of epoxy-amine

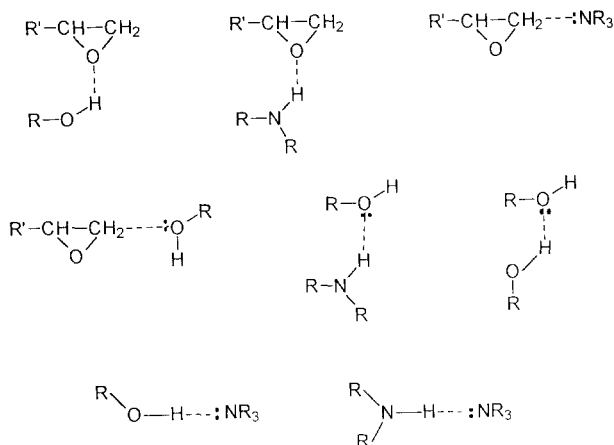
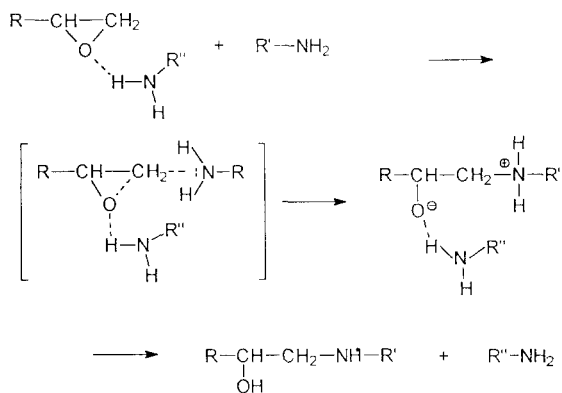


FIG. 1. Example of hydrogen bond complexes possible in an epoxy-amine system.

reactions as falling into two classes. The first being complexes that facilitate the reaction causing an accelerated rate, and the others being those that compete with species in the first class, reducing the concentration of other complexes and thus inhibiting the reaction. In systems with other electron-rich groups, such as the phenyl group in aromatic molecules, other complexes are possible and these can also inhibit the reaction. An inhibition effect has been observed<sup>15</sup> at high conversions for PGE-aniline in *o*-dichlorobenzene as solvent. This effect was found by Rozenberg<sup>15</sup> to be observed only when the basicity of the secondary and tertiary amine groups formed in the reaction was higher than that of the initial primary amine.

The addition reaction of secondary amine and epoxy groups (Scheme 2) is viewed as occurring by the same mechanisms as those just discussed for the primary amine-epoxy addition reaction. However, secondary amine groups are more sterically hindered towards reaction than primary amines resulting in a negative substitution effect on the reactivity of the amino hydrogen in secondary amines as compared to those in a primary amine. That is, the rate of reaction of an epoxy group with an amino hydrogen is slower when substitution on the nitrogen has occurred.

The magnitude, or indeed the actual occurrence at all, of such a substitution effect has remained controversial.<sup>15,16,17</sup> The effect is usually described by quoting the ratio



SCHEME 6.

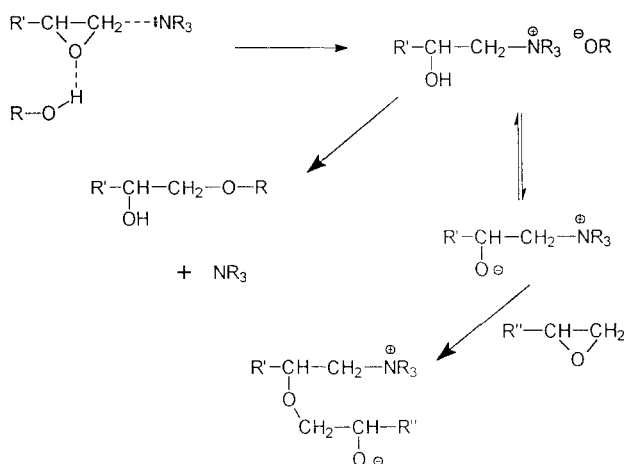
of the rate constants for secondary ( $k_2$ ) and primary ( $k_1$ ) amine reactions with epoxies. A ( $k_2/k_1$ ) value of 0.5 when group concentrations are used is viewed as representing no substitution effect owing to the primary amine group having two hydrogens and thus twice the probability of reacting compared to one hydrogen in a secondary amine. The ( $k_2/k_1$ ) values from different studies, using a variety of techniques, have been tabulated by several authors including Charlesworth,<sup>16</sup> Rozenberg<sup>15</sup> and recently by Mijovic *et al.*,<sup>17</sup> and show reported values varying from 0.1 to 1.0. The reasons for this wide variation are partly due to the different rate equations used to derive the rate constants and to the different epoxides and amines employed. However, even when one system is considered using the same method, a significant variation in results is observed. For example, PGE and aniline have been reported to have ( $k_2/k_1$ ) values varying from 0.25 to 0.44. One reason for this has been highlighted recently by the work of Buist *et al.*<sup>18,101</sup> using a radiochemical procedure to study the reaction of PGE–aniline. They found that ( $k_2/k_1$ ) was 0.44 for neat PGE–aniline while ( $k_2/k_1$ ) fell to 0.26 when ethanol was used as a diluent. Thus, the solvent appears not only to catalyze the amine-addition reaction, but does so to the primary amine reaction preferentially. This is probably due to the inhibition effect mentioned earlier.

The impetus for the large number of studies on this subject relates to the consequence of such a negative substitution effect on the cure of an epoxy–amine system. In the case of equal reactivity a randomly crosslinked structure should form. In contrast, if the primary amine hydrogens are much more reactive than the secondary amine hydrogens one would expect an initial predominance of linear chains followed by subsequent crosslinking resulting in a different network structure and perhaps different final properties. It is clear from all the studies undertaken that the strength of any substitution effect is dependent on several variables, including the system studied, the cure temperature and the presence of added diluents. Thus it is not possible to make any assumptions about the effect when studying the cure of a particular epoxy–amine system.

The etherification reaction (Scheme 3) is much slower than the amine addition reactions with epoxide at the cure temperatures normally used.<sup>12,15</sup> Epoxide reactions are generally catalyzed by tertiary amines and etherification reactions have been found to be catalyzed by the presence of tertiary amines of Lewis acids (e.g.  $\text{BF}_3$ : amine complexes). Several researchers have thus suggested an initial mechanism<sup>15</sup> shown in Scheme 7. The quaternary amine–alcoholate is fairly stable and thus can act as a propagating species in a ‘living’ anionic polymerization, or can just form the etherification product. Such complexes as those shown in Scheme 7 have been used to initiate the anionic polymerizations of acrylonitrile and caprolactone monomers by Ikeda and co-workers.<sup>20</sup> In epoxy–amine systems, etherification is so unfavoured compared to the amine-addition reactions that little chain growth by such a mechanism is likely unless a good catalyst is added.

## 2.2. Glycidyl amine model studies

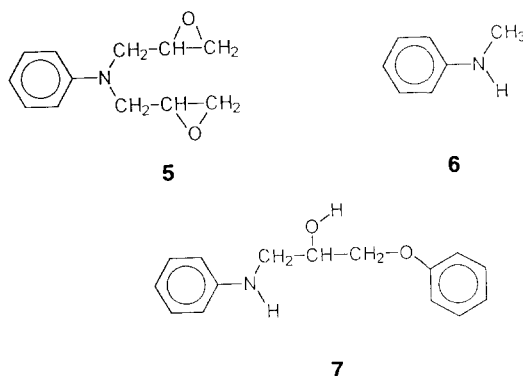
As discussed earlier a widely used glycidyl amine epoxy resin system is the tetrafunctional epoxide  $N,N,N',N'$ -tetraglycidyl-4,4'-diaminodiphenyl-methane (TGDDM – 1) and the aromatic diamine, 4,4'-diaminodiphenylsulphone (DDS – 2). This system is notable from a chemical standpoint for the high epoxy functionality of TGDDM and the low basicity, and thus low reactivity, of the amine groups on



SCHEME 7.

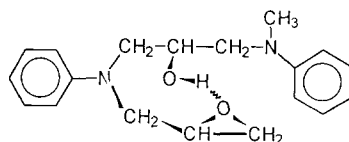
DDS. This results in a complex network structure and the need for high cure temperatures ( $>140^\circ\text{C}$ ).

In the last few years a considerable amount of work has been reported on the unique chemistry produced by the diglycidylanilino group (of which TGDDM has two) as opposed to the simpler glycidylether group in PGE and compounds like the diglycidylether of bisphenol A (DGEBA), which is also the basis of many commercial epoxy resins. Most of the studies have focused on model compounds which allow analysis of the reaction products by techniques such as High Performance Liquid Chromatography (HPLC), Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance spectroscopy (NMR).

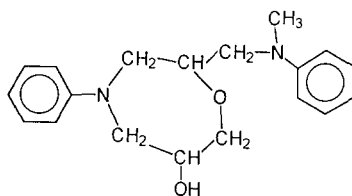


Matejka and Dusek studied the reaction at  $100^\circ\text{C}$  of diglycidylaniline (DGA) (**5**) with the secondary amines *N*-methylaniline (NMA) (**6**) and 1-anilino-3-phenoxy-2-propanol (**7**), separating the reaction products with HPLC and identifying them with NMR.<sup>21</sup> They observed that after one epoxy group of DGA had reacted with an amine, the adjacent epoxy group was 'activated' by the hydroxyl group formed, presumably via an intramolecular hydrogen bond as shown below (**8**). This positive substitution effect for the epoxy reaction was found to be greatest with NMA and was notable for both the epoxy-amine addition (1.5–8 fold increase in rate) and etherification reactions (3-fold increase in rate). The more sterically hin-

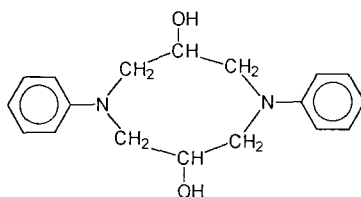
dered 1-anilino-3-phenoxy-2-propanol (**7**) showed a reduced epoxy substitution effect which was probably related to the presence of the hydroxyl group.

**8**

The rate of etherification was found to be an order of magnitude slower than the epoxy-amine reaction and that up to 60% of the etherification reaction, when epoxy was in excess, occurred intramolecularly producing the seven-membered ring 4-phenyl-2-(*N*-methylanilinomethyl)-1-oxa-4-aza-6-cycloheptanol (**9**).

**9**

In a further study Matejka and Dusek followed the reaction of DGA and aniline.<sup>22</sup> The reaction with the primary amine, aniline, showed a pronounced tendency towards ring formation. Eight-membered rings, 3,7-dihydroxy-perhydro-1,5-diazocines (**10**), were formed by reaction of the secondary amine produced in the initial primary amine epoxy-addition with the adjacent epoxy group on the same molecule. This product was formed from the very early stages of reaction and its formation was comparable with that of linear oligomers (i.e. intermolecular reaction). Ether cycles, which would have been present in small amounts, were unable to be identified in this reaction as the product was much more complex.

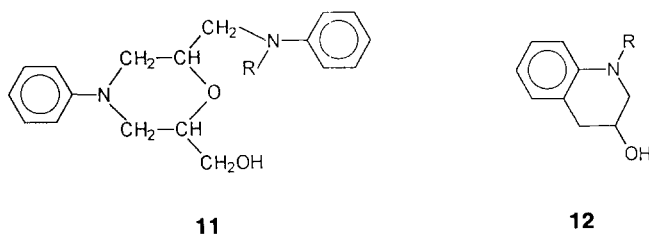
**10**

The studies<sup>21,22</sup> were summarized by noting that the mechanism and kinetics of the reaction of DGA with aromatic amines are considerably more complicated than those of glycidylether epoxides like DGEBA with: (1) the reactivity of all functional groups being mutually dependent; (2) a great tendency towards intramolecular reactions producing small cycles; and (3) etherification being more pronounced. In a recent study Matejka *et al.*,<sup>23</sup> reported that the degree of cyclization in the reaction of DGA with aniline is dependent on stoichiometry and increases with increasing temperature and upon dilution of the reaction mixture with an inert diluent.



Johncock and co-workers recently studied the reaction of DGA with aniline and substituted anilines at temperatures up to 200°C.<sup>24,25</sup> They concluded that the 8-membered diazocine ring (**10**) was the dominant intramolecular cyclization product. By studying substituted anilines they found that steric effects were more important than polar effects in determining the extent of cyclization. Yields of the 8-membered cyclic product from the reaction of DGA comprised 15% of the reaction products with aniline and 45% with 2,6-dimethylaniline.<sup>24</sup>

Two intramolecular reaction products were also identified in addition to the diazocine ring and 7-membered ether ring similar to structure **9**.<sup>25</sup> These were the morpholine ring product (**11**), produced by intramolecular etherification like the 7-membered ether ring, and a 1,2,3,4-tetrahydro-3-hydroxyquinoline ring product (**12**) produced by a backbiting reaction which will be discussed in more detail later.

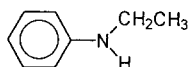


The two etherification products (**9** and **11**) represented 4 and 6%, respectively, of the consumed epoxy groups in the reaction of DGA with aniline at 176°C.<sup>25</sup> The hydroxyquinoline (**12**) represented about 3% in the same mixture. Contrary to the amine cyclization reaction, the ether cyclizations were found to be largely influenced by electronegative substitutions on aniline with only a small effect from steric hindrance.<sup>25</sup> This was reflected in a yield of 28% ether cycles when 2,4,6-trichloroaniline was used instead of aniline which produced 10%.

A polymeric species produced by reacting DGA with aniline had a molecular weight of about 3000 and <sup>13</sup>C NMR showed no branching, indicating few intermolecular etherification reactions. This is contrary to observations of Matejka *et al.* which found that 40% of the ether products in essentially the same reaction were not involved in cyclic structures. Two new thermal reactions were proposed to explain the <sup>13</sup>C NMR and GPC results for the produced polymer after heating to 220°C. As shown in Scheme 8, these were: a chain cleavage giving a 1,2,3,4-tetrahydro-3-hydroxyquinoline and a secondary amine chain end; and an elimination of water from adjacent hydroxyl groups to produce an in-chain morpholine ring.

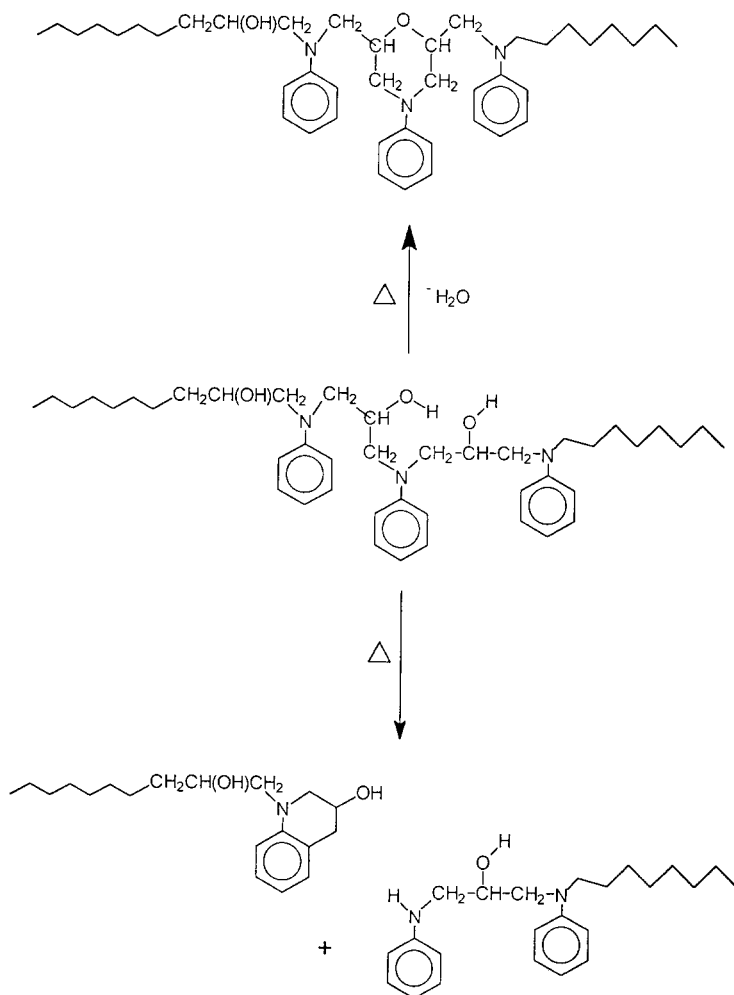
Attias *et al.*<sup>26</sup> carried out a detailed study using GPC and <sup>13</sup>C NMR of the products of the reaction of DGA with the secondary amine, *N*-ethylaniline (**13**). By synthesizing model compounds, a positive identification of the intramolecular etherification products analogous to structures **9** and **11**, and the 1,2,3,4-tetrahydro-3-hydroxyquinoline product analogous to structure **12** in the reaction products was made. They were the first to recognize the back-biting reaction of *N*-glycidylanilino groups to form the hydroxyquinoline rings. These structures have since been identified by other groups.<sup>22,25</sup> Such cyclic products were observed earlier by Davies and Savige as the product of the reaction of an aromatic secondary amine with epichlorohydrin at high temperatures.<sup>27</sup> A mechanism, shown in Scheme 9, has been proposed for the backbiting reaction. Attias *et al.* found no evidence for intermolecular etherification<sup>28</sup>

and so concluded that intermolecular etherification did not occur or was very slow under their conditions.

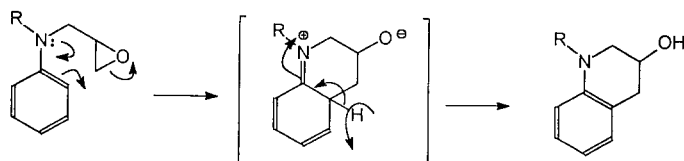


13

Matejka, Podzimek, Dusek and co-workers have concentrated recently on the ether forming reactions of *N*-glycidylanilines.<sup>29</sup> The model compounds they used

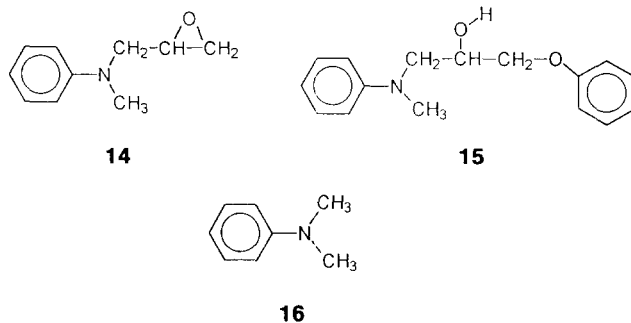


SCHEME 8.



SCHEME 9.

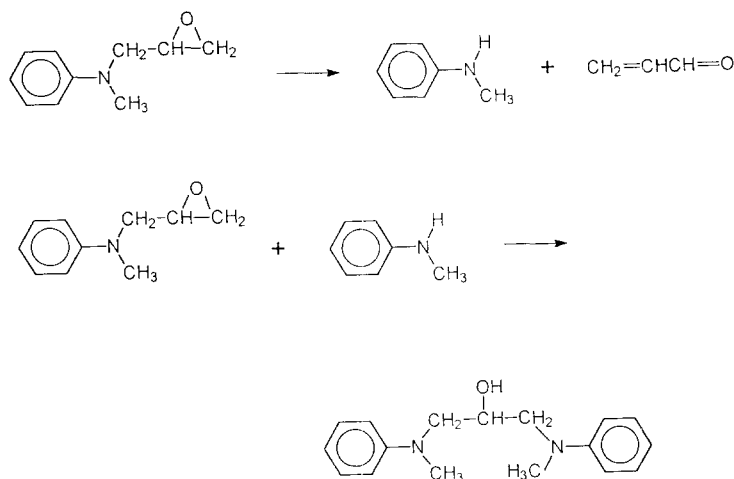
were *N*-methylglycidylaniline (NMGA), (**14**), 1-phenoxy-3-(*N*-methylanilino)-2-propanol (**15**) and the tertiary amine *N,N*-dimethylaniline (DMAN), (**16**). By using these compounds, intramolecular cyclizations are not possible allowing the intermolecular etherification reactions to be investigated. All reactions were carried out in the temperature range 100–170°C.



The reaction of NMGA with DMAN as catalyst or with (**15**) formed, as the major products, 1,3-di(*N*-methylanilino)-2-propanol and a number of low molecular weight oligomers. The formation of the first product was explained by the pathway shown in Scheme 10; *N*-methylaniline (**6**) was identified in the reaction mixture, however, acrolein was not identified amongst the products.

The oligomers were found to be formed by two different mechanisms. The first was direct etherification with reaction of epoxy groups with hydroxyl groups which were present in (**15**), products of previous reactions and diols formed by trace water. The second mechanism involves an anionic chain mechanism initiated by DMAN in a manner similar to that shown previously in Scheme 7. Taking account of all possible reaction paths presented by the two mechanisms, a complex kinetic scheme was derived with seven independent rate constants.<sup>29</sup>

The fraction of oligomers in the products did not exceed 40% and their molecular weights were low ( $M_n < 600$ ). Both the weight fraction of oligomers and their



SCHEME 10.

molecular weights decreased with increasing concentration of compound **15**. This supports the view that the etherification reactions are dominant when hydroxyl groups are present and the anionic chain mechanism occurs predominantly when hydroxyl groups are absent or are present in low concentrations.

It can be noted that there has been a large amount of detailed work on model systems for epoxy-amine cure and these have revealed a variety of possible reaction products, especially for the class of epoxides containing *N*-glycidylanilino groups. These results can be summarized by the following points:

(i) Primary amine reactions with epoxide are catalyzed by species capable of hydrogen bonding, including primary amines and the hydroxyl groups produced in the addition reaction.

(ii) Secondary amine reactions with epoxide occur in a similar way to primary amines, though often at a significantly slower rate due to a negative substitution effect which is most likely caused by steric hindrance.

(iii) Hydroxyl reactions with epoxide (etherification) occur only at elevated temperatures and are favoured by the presence of tertiary amines.

(iv) *N*-glycidylanilino compounds, on reaction with aromatic amines, give rise to several cyclic structures not seen for other epoxides. Reaction with primary amines yields an 8-membered ring through a follow-on intramolecular secondary amine-epoxy addition reaction which is enhanced by steric hindrance on the secondary amine. Morpholine and 7-membered ether rings are formed and these are favoured by electrophilic substitution on the aromatic ring. A back-biting reaction also occurs producing a 1,2,3,4-tetrahydro-3-hydroxyquinoline ring.

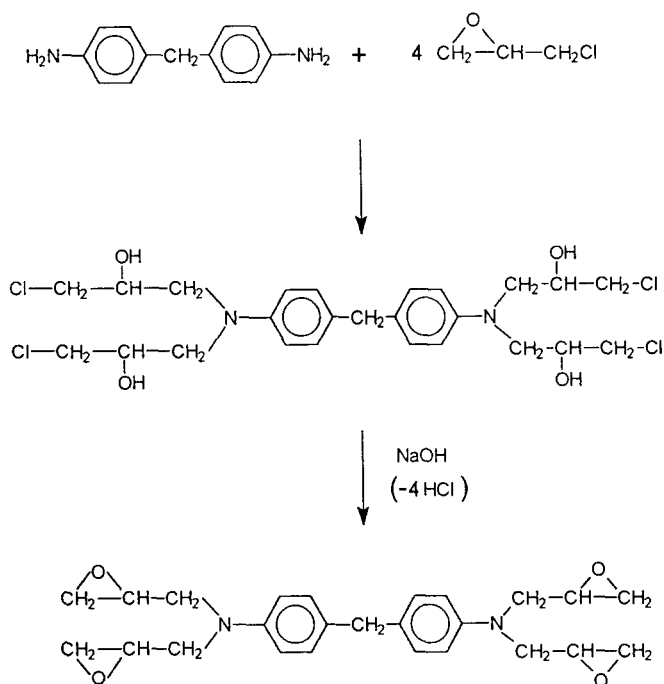
(v) *N*-diglycidylanilino compounds, after one epoxy group has reacted, exhibit a positive substitution effect on the reactivity of the remaining epoxy group, presumably through activation by the hydroxyl group formed in the first reaction.

(vi) In *N*-glycidylanilino compounds, little chain growth occurs due to etherification or an anionic growth mechanism, especially when hydroxyl groups are present.

Even though there are essentially three basic types of reactions involved in the cure of an epoxy-amine system, any kinetic scheme used to describe the cure must be fairly complex to accurately reflect all of the different reaction paths possible in such a system. Of particular interest is the extent to which the results of model compound studies may be applied to the more complex difunctional or tetrafunctional epoxy resins and hardeners.

### 3. GLYCIDYL AMINE EPOXY RESINS

There have been several different glycidyl amine epoxy resins described in the literature. For example, many structural adhesives have incorporated a trifunctional mixed glycidyl ether-glycidyl amine resin – Ciba Geigy ERL0510 (triglycidyl 4-aminophenol) – to achieve a high crosslink density.<sup>19</sup> In contrast, a lower crosslink density resin in Shell 1071<sup>4</sup> which is an extended aromatic version of the most widely studied glycidyl amine resin – TGDDM (**1**). Because of the large amount of research which has been carried out on the various commercial forms of TGDDM and its incorporation into advanced composite materials, only this resin will be considered in the following sections.



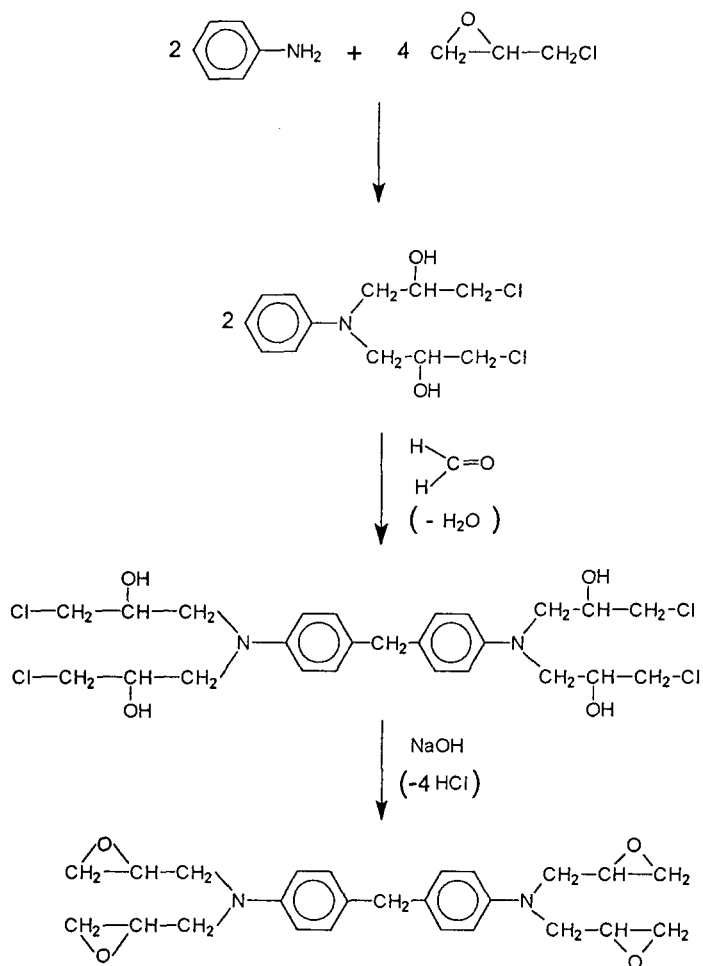
SCHEME 11.

### 3.1. Synthesis of TGDDM

There are two reaction sequences recognized as being suitable for the synthesis of TGDDM, both of which involve several steps. These are unlike the manufacture of glycidyl ether-based resins which can be carried out in a single synthetic step.<sup>30</sup>

The most commonly used reaction sequence for the manufacture of TGDDM involves, as shown in Scheme 11, reacting 4,4'-diaminodiphenylmethane (DDM) portionwise with a slight excess of epichlorohydrin to yield a chlorohydrin which is subsequently dehydrochlorinated with sodium hydroxide to yield epoxy groups. This scheme has the advantages that it involves essentially only two synthetic steps and DDM is highly reactive, as well as being a readily available and inexpensive starting material.<sup>31</sup> These reasons are partly why TGDDM has become the most commonly used glycidylamine epoxide.

The other reaction sequence involves three synthetic steps, as shown in Scheme 12, and uses aniline as the starting material which is reacted with epichlorohydrin to yield the dichlorohydrin. The next step involves condensation of this product with formaldehyde to yield the chlorohydrin precursor of TGDDM. The final step is the same as that for Scheme 11 where dehydrochlorination is carried out with sodium hydroxide.<sup>30</sup> This method has the advantage of allowing modification of the structure of the epoxide produced by substituting a ketone or aldehyde in place of formaldehyde to yield a different bridging unit between the two phenyl rings. Liu *et al.*<sup>32</sup> applied a variation of this by reversing steps 1 and 2 of Scheme 12 producing the diphenylamine first, and managed to produce a range of epoxies with ethyl, methyl and propyl groups substituted on the bridging carbon, as well as obtaining TGDDM, by using the appropriate carbonyl compound.

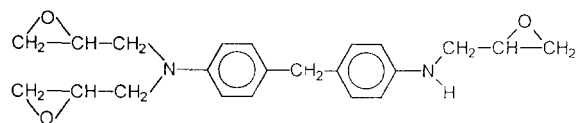
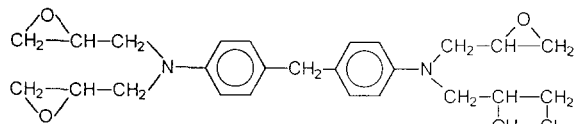
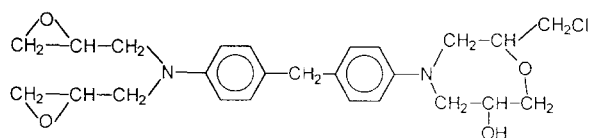
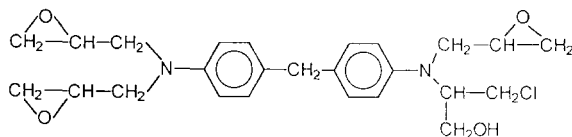
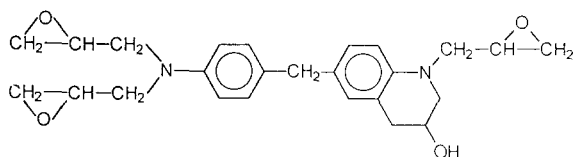


### 3.2. Impurities in commercial TGDDM resins

In any multiple step synthesis, it is difficult to obtain a pure substance in reasonable yield and the manufacture of TGDDM on a commercial scale results in a variety of impurities being present in the final product. The variation of the overall level of impurities from one batch to another at the stage at which fibres are impregnated with epoxy resin to form prepreg makes reproducible fabrication of composite parts difficult.

Podzimek *et al.* carried out a detailed analysis using HPLC, GPC and NMR of by-products from both reaction sequences described in the previous section for the manufacture of TGDDM.<sup>30,33</sup> The first reaction sequence starting with DDM as the precursor (Scheme 11) was found<sup>33</sup> to yield, as well as TGDDM, the partially reacted intermediates *N,N,N'*-triglycidyl-4,4'-diaminodiphenylmethane (17) and *N,N,N'*-triglycidyl-*N'*-(2-hydroxy-3-chloropropyl)-4,4'-diaminodiphenylmethane (18) and its homologues (19 and 20), the 1,2,3,4-tetrahydro-3-hydroxyquinoline compound (21), the dimer (22) and higher oligomers. Grenier-Loustalot and Grenier also investigated the by-products in this synthetic route<sup>42</sup> and reported similar findings except that they

also identified the presence of diols which are produced by the hydrolysis of epoxy groups. All of these impurities are consistent with the chemistry that these types of compounds undergo as described in Section 2.2.

**17****18****19****20****21**

Podzimek *et al.* found that when the second synthetic route (Scheme 12) was employed,<sup>30</sup> the by-products generated differed from those obtained with the first method in that: a higher content of the 1,2,3,4-tetrahydro-3-hydroxyquinoline compound (**21**) was produced; the oligomers appeared to have a different structure; and a new by-product, compound **23**, was identified.

Several companies now manufacture TGDDM resins with all showing different impurity profiles.<sup>34,45</sup> The most widely studied commercial TGDDM resins are MY720 and MY721, produced by Ciba-Geigy. HPLC was used to analyse MY720, MY721 and a purified form of TGDDM derived using flash chromatography on MY721.<sup>5</sup> The typical chromatograms obtained are shown in Fig. 2 and were similar to those obtained by King *et al.*<sup>35</sup> and Hagnauer *et al.*<sup>6</sup> The HPLC peaks can be compared to those obtained by Podzimek *et al.*<sup>30,33</sup> and Grenier-Loustalot *et al.*<sup>34</sup> and are partitioned into three groups as indicated in Fig. 2.

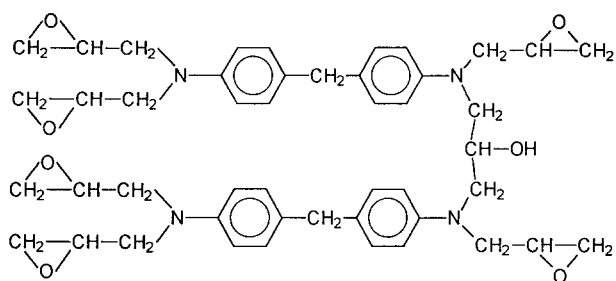
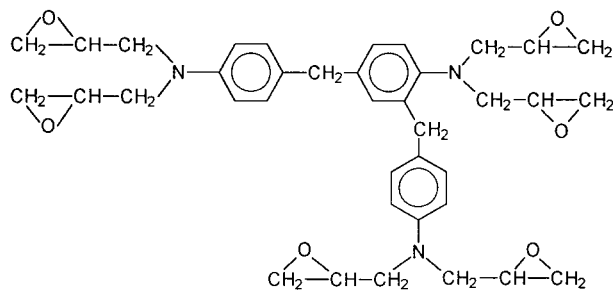
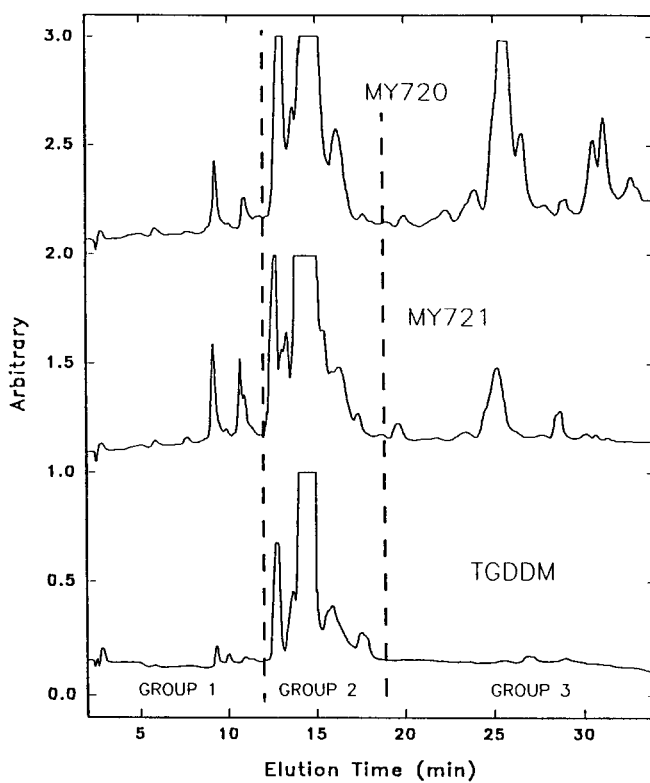
**22****23**

FIG. 2. HPLC chromatograms for MY720, MY721 and purified TGDDM.



TABLE 1. Epoxy content of TGDDM resins

Resin	% TGDDM monomer	Epoxy equivalent weight	Epoxy concentration (mol · kg <sup>-1</sup> )
MY720	63	125	7.9
MY721	79	110	9.10
TGDDM	93	106	9.48

Group 1 peaks represent the more polar components including the partially reacted starting material (**17**), the 1,2,3,4-tetrahydro-3-hydroxyquinoline product (**21**) and simple glycols. The peaks in group 2 include the TGDDM monomer and associated chlorohydrin impurities (species **18**, **19** and **20**). The remaining impurities in group 3 include the dimer (**22**) and other higher oligomers. Table 1 summarizes the epoxy content obtained for the three samples. The average number of epoxy groups in each impurity is near three except for the higher oligomers where it is lower. This is why a high epoxy concentration can be obtained even with fairly low TGDDM monomer content as indicated in Table 1.

It is clear from the HPLC chromatograms that MY720 has a significant level of dimer and higher oligomers which result in a higher viscosity and lower epoxy content than MY721.<sup>36</sup> On the other hand, although the overall level of impurities for MY721 is lower than that for MY720, chlorohydrin impurities and species **17** and **21** are present in significant amounts. The purified MY721 showed predominantly TGDDM monomer as would be expected.

The consequences of the presence of impurities are essentially twofold in that the stability of the resin is reduced and the cure kinetics of the resin are altered. Hagnauer and Pearce<sup>6</sup> examined the hydrolytic stability of MY720 and a purified TGDDM resin and found the purified resin to be considerably more stable. This suggests that hydrolysis may be catalyzed by hydroxyl impurities. They also reported that the rate of reaction as measured by DSC was increased by the presence of impurities. In a more recent study Podzimek *et al.*<sup>37</sup> examined the effects of impurities on the shelf-life of TGDDM-based resins and determined that hydroxyl containing impurities critically affected shelf-life. The consequence of deterioration of TGDDM resins is that the viscosity increases, affecting processibility and the cure chemistry is altered, resulting in an altered network structure. Therefore, it is important to be cognizant of the level and influence of impurities in TGDDM resins. This is discussed later (Section 5).

#### 4. KINETIC ANALYSIS OF THE CURE OF TGDDM WITH DDS

As discussed in Section 2.2, much of our understanding of reactions in glycidyl amine-based epoxy resins has been gained through studies with monofunctional epoxides reacted with monofunctional primary or secondary amines. Particular kinetic parameters for the reaction of these models as well as the identification of the reaction products have been determined by measurement of concentration changes as a function of reaction time using HPLC, GPC and NMR. All of these techniques require the reactants and products to be soluble in common solvents and this is readily achieved if the products are of low molecular weight. However when a tetra functional resin such as TGDDM is reacted with the tetrafunctional amine such

as DDS, there is an increase in molecular weight followed by crosslinking which renders the products insoluble. In spite of this, the **initial** rates of reaction have been measured by HPLC<sup>6</sup> and <sup>13</sup>C NMR<sup>34</sup> has been used to provide structural information up to the point of gelation. Some additional structures have been identified by solid state NMR at later stages of reaction, but, as discussed later (Section 4.3) the broad NMR bands preclude definitive assignments. In the analysis of cure kinetics of epoxy resins over a wide range of conversions, DSC has often been the technique of choice because of the experimental simplicity.<sup>38</sup> Infrared spectroscopy<sup>2</sup> (particularly in the near-infrared region)<sup>5</sup> has complemented DSC in providing functional group information during crosslinking and has offered the greatest insights into the cure kinetics of commercial resin systems at conversions where product analysis by HPLC and NMR is impossible.

#### 4.1. *Differential scanning calorimetry*

Reactions involving epoxy ring opening are highly exothermic, as reflected in the risk of thermal runaway in epoxy cure reactions.<sup>10</sup> Thus Differential Scanning Calorimetry (DSC) was recognized very early as a valuable tool in the study of the cure of epoxy resins. Barton<sup>38</sup> evaluated DSC as a method for monitoring the cure of epoxy resins and concluded that it is an effective technique, particularly when combined with spectroscopic, chromatographic and rheometric analyses. It is not surprising then that a commercially important resin system like TGDDM/DDS has been the subject of many DSC studies.

There are essentially two types of experiments that can be carried out on a DSC instrument. One is an isothermal experiment where temperature is maintained at a constant value and the other is a 'dynamic' experiment which involves ramping the temperature at a constant rate to a predetermined value. The two types of experiments are distinctly different in the information they can provide on reaction kinetics. Both have been used extensively for the study of the cure in TGDDM/DDS systems.

The isothermal experiment yields values for the rate of energy release vs time ( $dH/dt$ ) at constant cure temperature. These values are assumed to be directly related to the reaction rate,  $d\alpha/dt$ , where  $H$  represents the energy of the system and  $\alpha$  is the extent of reaction with  $\alpha = 1$  representing complete reaction. If the total energy change in the system for full cure ( $H_{tot}$ ) is known, then the reaction rate can be determined as shown in Eq. 1.

The integrated form, with respect to time, of the isothermal DSC curve will then yield values for extent of reaction vs cure time. However, several assumptions are required if DSC is to be used in this way. The most important is that  $H_{tot}$  can be accurately determined. For TGDDM/DDS where complete reaction does not occur at the cure temperatures normally used,  $H_{tot}$  is usually determined by carrying out a dynamic DSC scan to high temperatures after the isothermal run and adding this heat obtained to the total isothermal value. The other major assumption is that all reactions contributing to the consumption of the species in question have the same reaction enthalpy.

$$d\alpha/dt = 1/H_{tot} \cdot dH/dt \quad (1)$$

Several workers have analysed the cure of TGDDM/DDS in this way<sup>8,39-43</sup> and have examined the obtained extent of reaction curves in an attempt to derive reaction

kinetics. Most workers have made an unsupported assumption that the enthalpy of all epoxide reactions is equal, citing the close agreement for total heats of reaction from dynamic DSC scans for different stoichiometries and different epoxy resins. This assumption allows one to fit kinetic equations to the rate or extent of reaction curves.

Horie *et al.*<sup>44</sup> derived a kinetic relationship for epoxy-amine cure assuming near equal reactivity of primary and secondary amines and no other reactions. This was later refined by Sourour and Kamal<sup>45</sup> and takes the form of eq. 2 for a stoichiometric epoxy-amine system:

$$d\alpha/dt = (k_1 + k_2\alpha)(1 - \alpha)^2 \quad (2)$$

where  $k_1$  and  $k_2$  are Arrhenius-type rate constants representing the so-called 'non-catalytic' and 'autocatalytic' features of the kinetics, respectively. Barton<sup>8</sup> found this equation to be inappropriate for TGDDM/DDS and so applied the more general empirical equation, eq. 3:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (3)$$

where  $m$  and  $n$  are adjustable parameters representative of the order of the individual terms. Barton obtained a fit using ( $m = n = 1$ ) over the first 30% of conversion and interpreted this using Horie's method<sup>45</sup> as implying that the dominant reaction mechanism is bimolecular. However, the limited extent of conversion over which this equation remains useful undermines any conclusions that can be made concerning mechanism.

Mijovic<sup>39,40</sup> analysed the cure of TGDDM/DDS using the same equation (eq. 3) except that he allowed  $m$  and  $n$  to have any value as long as  $m + n = 2$ . The range of the fit was slightly improved, though kinetic interpretation of the results seems pointless since the values obtained for  $m$  and  $n$  varied from one temperature to another. Lee, Chiu and Lin<sup>41</sup> recently modified this approach by introducing a separate exponent,  $l$ , for the non-catalytic concentration term as shown below in eq. 4:

$$d\alpha/dt = k_1(1 - \alpha)^l + k_2 \cdot \alpha^m(1 - \alpha)^n \quad (4)$$

For TGDDM/DDS they used values of  $l = 2$  and  $m + n = 2$  and were able to obtain a good fit for their DSC data for up to 70% conversion after which they suggested that diffusion control of the reaction rate became dominant. The difficulty with this type of approach is that for each resin, it is necessary to determine not only new pseudo rate constants but also new values for the exponents.<sup>39,41</sup> This supports the view that these exponents are more akin to curve fitting parameters and not a true reflection of the underlying reaction mechanisms involved.

Grenier-Loustalot and Grenier<sup>34</sup> used Calvet microcalorimetry, which is a technique similar to DSC, to analyse the cure in TGDDM/DDS resins and fitted their experimental conversion data using a rate law of the form shown in eq. 5, where  $R$  and  $D$  are concentrations of epoxy and amine and  $X$  is the concentration of the product of the reaction ( $R + D \rightarrow X$ ) which is in effect the hydroxyl concentration.

$$-dX/dt = k_1(R - X)(D - X) + k_2 \cdot X \cdot (R - X)(D - X) \quad (5)$$

Though this equation more closely follows the expected kinetic form and is similar to that of Horie *et al.*,<sup>45</sup> no examples of the quality of fit are presented and the conversion data were scaled using the total heat of reaction determined on a different instrument

(a DSC). It is therefore not possible to judge the reliability of their results considering they contradict Barton's observations from his DSC studies that an equation of this form is unsuitable for the TGDDM/DDS system.

A different approach for analysing isothermal DSC data has been to derive rate expressions that encompass all of the expected mechanistic features for an epoxy-amine cure including the substitution effect on amine reactivity and etherification reactions. The earliest use of this approach for TGDDM/DDS was by Zukas *et al.*,<sup>42</sup> who assumed the following rate law shown in eq. 6:

$$\begin{aligned}
 -d[\text{EP}]/dt = & k_1[\text{PA}][\text{EP}] + k_2[\text{SA}][\text{EP}] + k_3[\text{OH}][\text{EP}] \\
 & + k_4[\text{PA}][\text{EP}][\text{OH}] + k_5[\text{SA}][\text{EP}][\text{OH}] + k_6[\text{OH}][\text{EP}][\text{OH}] \quad (6)
 \end{aligned}$$

where [EP], [PA], [SA] and [OH] are epoxy, primary amine, secondary amine and hydroxyl group concentrations. From this, an expression was derived assuming that the ratio of rate constants for primary and secondary amine addition is a constant,  $\beta$ , and is the same ratio for the autoaccelerated reactions (i.e.  $\beta = k_1/k_2 = k_4/k_5$ ). Also, it was assumed that the ratio of etherification reactions to primary amine-epoxy addition reactions is constant (i.e.  $\gamma = k_1/k_3 = k_4/k_6$ ). However, they found that their DSC data was insensitive to the variable  $\gamma$  for TGDDM/DDS and so were unable to obtain values for the extent of etherification reactions. To obtain a reasonable fit to their DSC data, they found it necessary to include an order for the hydroxyl terms of 1.25 and a variable order for epoxy concentration dependence with an initial value of zero increasing linearly to 0.5 at 100% conversion. Clearly, such modifications contradicted any mechanistic approach to the kinetics with an initial order for epoxy of zero, suggesting that the rate law used (eq. 6) was incorrect.

Chiao also adopted a mechanistic approach<sup>46</sup> and used as the basis for his calculations the following rate law in eq. 7:

$$\begin{aligned}
 -d[\text{EP}]/dt = & k_1[\text{PA}][\text{EP}] + k_2[\text{SA}][\text{EP}] + k_3[\text{PA}][\text{EP}][\text{OH}] \\
 & + k_4[\text{SA}][\text{EP}][\text{OH}] + k_5[\text{OH}][\text{EP}] \quad (7)
 \end{aligned}$$

where the concentration terms have the same meaning as in eq. 6. Chiao also assumed that the ratio of hydroxyl catalyzed and uncatalyzed rate constants was the same for both primary and secondary amine addition giving essentially three independent rate parameters. By numerically solving the rate expressions he was able to generate individual group concentrations at different extents of reaction for any set of rate constants.

Chiao used this method to analyse Morgan and Mones<sup>9</sup> FTIR results for TGDDM/DDS with  $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$  catalyst<sup>7</sup> and Mijovic *et al.*'s DSC results for TGDDM/DDS.<sup>40</sup> A good fit was obtained for Mijovic *et al.*'s results for 22 wt% DDS with, for example at 150°C,  $k_3$ ,  $k_4$  and  $k_5$  equal to  $6.71 \times 10^{-3}$ ,  $3.09 \times 10^{-4}$ , and  $7.95 \times 10^{-4} \text{ l}^2 \text{ mol}^{-2} \text{ min}^{-1}$  respectively. It is interesting to note the large substitution effect on amine reactivity apparent from these results with  $k_4/k_3$  (usually quoted as  $k_2/k_1$ ) being 0.046. Good Arrhenius plots were also obtained for this stoichiometry. However when the obtained constants were used to calculate conversion curves for 19 wt% and 27 wt% DDS, there was a significant difference in comparison to the DSC data, though the same trends were observed over the course of the cure.

Recently, Cole<sup>47</sup> used a similar approach basing his analysis on the assumed mechanistic rate expression provided in eq. 8 below:

$$-d[\text{EP}]/dt = k_1[\text{PA}][\text{EP}][\text{X}] + k_2[\text{SA}][\text{EP}][\text{X}] + k_3[\text{PA}][\text{EP}][\text{OH}] + k_4[\text{SA}][\text{EP}][\text{OH}] + k_5[\text{EP}][\text{OH}]^m[\text{TA}]^n \quad (8)$$

where [X] represents the concentration of catalytic impurities, [TA] represents the concentration of tertiary amine groups,  $m$  and  $n$  are reaction orders to be determined and the other terms have the same meaning as for eqs 6 and 7. It is apparent that Cole replaced Chiao's 'uncatalyzed' terms with impurity catalyzed terms which has no effect on the mathematical form of the relationships as [X] is assumed to be constant. To obtain an exact solution for individual group concentrations during cure it was assumed that no substitution effect occurred for the secondary amine reaction (i.e.  $k_3 = 0.5k_4$ ). This allowed expressions using rate constants and initial concentrations to be derived for three independent constants that could be used to describe the cure reaction.

Cole *et al.*<sup>43</sup> used this derivation to analyse their isothermal DSC data for the TGDDM/DDS commercial resin Narmco 5208. They found a best fit when the orders for the etherification term were 1 for epoxy, hydroxyl and the tertiary amine groups produced by reaction of secondary amine groups on the DDS units (i.e.  $m = n = 1$ ). To model the retardation towards the end of cure associated with vitrification, they used a semi-empirical relationship previously derived by Chern and Poehlein<sup>48</sup> for a different epoxy resin. Using their model, an excellent fit over the entire cure was obtained at six different temperatures from 160 to 210°C with the fitted rate parameters obeying an Arrhenius relationship.

These results demonstrated the power of a mechanistic approach for the study of the cure kinetics of epoxy-amine systems. It is unfortunate from a mechanistic viewpoint that the existence and extent of a substitution effect for the secondary amine reaction was unable to be ascertained by the approach used. Also, as with other DSC studies, the assumption of equal reaction enthalpies for all epoxy reactions had to be made resulting in some underlying uncertainty in their conclusions. Nonetheless, the methodology described represented a major advance in the use of isothermal DSC for the study of cure kinetics. More recently a combined FT-IR-DSC method was employed to examine these assumptions and limitations.<sup>49</sup> This is discussed in greater detail in Section 4.6.

Dynamic DSC as a technique for studying the cure of thermosetting resins has the attraction that the experimental runs are short and the results from one run are reputed to be able to yield all the Arrhenius parameters necessary to describe the kinetics for a particular sample. Most of the approaches used to achieve this are based on the method originally proposed by Borchardt and Daniels<sup>50</sup> which assumes a constant heating rate and derives kinetic parameters from step integrals of the DSC curve. Kissinger<sup>51</sup> derived a relationship using multiple heating rates to obtain the Arrhenius parameters from the temperatures of the exotherm maxima.

The difficulty with both of these approaches is that they assume that only one reaction mechanism and thus one set of kinetic parameters is operable over the entire range of temperatures scanned. Also it is implicit in such methods that the rate of reaction at any point during the cure is independent of the degree of cure that has already occurred, that is to say any effects of diffusion control are negligible. Considering: (1) that even at a single temperature an epoxy-amine system potentially

can undergo several different reactions; (2) that above 200°C different reaction mechanisms start to dominate for TGDDM; and (3) an extensive network structure quickly develops in a system like TGDDM/DDS, then it would seem that such methods would be of little value for the study of epoxy-amine systems.

Barton,<sup>8</sup> recognizing the unsuitability of the technique, found when using a modification of Kissinger's method which compared cure rates to temperature at constant conversion using multiple heating rates, that for TGDDM/DDS he obtained good linearity for his plots. However, the derived activation energies increased with conversion which supports the view that increasing conversion restricts reaction through diffusion control.

Apicella *et al.*<sup>52</sup> used dynamic DSC to analyse a range of different stoichiometries of TGDDM/DDS from 50 wt% DDS to 0 wt% DDS in TGDDM. They assumed that in neat TGDDM only homopolymerization occurred and in the 50 wt% DDS sample only primary amine-epoxy addition occurred when subjected to heating rates of 10 and 20°C · min<sup>-1</sup> up to 300°C. Thus they reasoned that the Arrhenius parameters for the two individual reactions could be determined. By making the additional assumption that the secondary amine-epoxy addition reaction was negligible in the cure of TGDDM/DDS, they asserted that the kinetics for any stoichiometry could be determined by a suitable proportioning of the two reactions. However, in their reported example, the calculated conversion curve for 35 wt% DDS at 180°C significantly overestimated the extents of conversion compared to experimental results obtained using isothermal DSC. This was not surprising considering the severe assumptions that were made about the likely reactions involved. By using a simultaneous DSC-FT-IR analysis (Section 4.6) for the concentration of functional groups and heat flow during a scanning experiment on TGDDM/DDS from 2° to 20°C min<sup>-1</sup>, it was demonstrated that there was a lag between the DSC reaction rate and the absolute reaction rate.<sup>53</sup> This deviation increased with heating rate and was attributed to the heat transfer coefficient of the sample which is not explicitly included in the kinetic analyses of the scanning DSC data.<sup>38,51</sup> It was suggested that the 'reaction order' and 'Activation Energy' obtained from dynamic DSC analysis was of no fundamental use because of this inherent limitation.

It should be noted that though the value of dynamic DSC as a tool in fundamental kinetic studies is doubtful, it has still found wide use as a purely empirical technique for the study of commercial resin systems. This is done by assuming the empirical relationships derived from isothermal DSC studies and calculating a set of Arrhenius parameters by fitting a dynamic DSC curve for a particular system. The advantage of this approach is that it provides thermodynamic and conversion data quickly that is not available otherwise which can then be used in modelling other property changes during cure (e.g. viscosity). Ciriscioli and Springer have used such thermochemical parameters in the development of their models for the 'smart' autoclave cure of composites.<sup>10</sup>

Letton and Chiou<sup>54</sup> have recently developed an approach for the catalyzed TGDDM/DDS based commercial resin Hercules 3501-6 using dynamic DSC. They deconvoluted the dynamic DSC curve into three component peaks using a thermal aging method and performed a multiple linear regression on each peak assuming the empirical expression, eq. 9, described the underlying kinetics.

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (9)$$

They found that when the kinetic parameters thus determined were used to calculate isothermal conversion curves, there was surprisingly poor agreement with the results obtained using isothermal DSC. It was acknowledged that it is the seldom documented inability of dynamic kinetic parameters to predict isothermal kinetics that needs to be seriously addressed. However, they were able to obtain reasonable isothermal curves if a different set of activation energies (obtained using Kissinger's method) were used while retaining the reaction orders and pre-exponential factors obtained before. Using these results they modelled the changes in viscosity during cure over a typical temperature program and obtained excellent correlation with actual viscosity measurements.

It is clear that dynamic DSC can be employed for modelling as long as it is recognized that the parameters obtained are essentially empirical curve-fit values and, though usually obeying an Arrhenius type relationship, do not reflect the underlying reaction mechanisms. The consequence of this is that it is not possible to adjust values for differences that may occur due to batch variation. DSC has remained an important technique for the study of epoxy–amine (and in particular TGDDM/DDS) cure kinetics despite the uncertainties attached to the various assumptions made. However, to understand properly the fundamental reaction kinetics in a complex system like TGDDM/DDS, a technique that is able to distinguish different chemical processes is necessary.

#### 4.2. Chromatographic analysis of the early stages of cure

Liquid chromatography techniques are routinely used for both the purification and analysis of uncured epoxy resins.<sup>1</sup> As described in Section 2, HPLC and GPC have played an important role in model studies of epoxy–amine reactions. However, the main limitation of both techniques is that only substances that can be dissolved in an appropriate solvent can be analysed. This means that once gelation occurs, analysis is not possible, thus restricting the study of crosslinking systems to pre-gelation conversions.

Halpin, Apicella and Nicolais investigated the cure of TGDDM with 26 wt% DDS at 180°C using HPLC.<sup>55</sup> They were able to monitor the change during cure in the concentrations of DDS and TGDDM, as well as the 1 : 1 and the 2 : 1 reaction products with less accuracy. The DDS was found to be completely reacted after 35 min which corresponded to the observed gel time. They drew no conclusions about the reaction kinetics, however it is of interest that their results show that over 20% of the initial TGDDM was still completely unreacted (i.e. still monomer) at the onset of gelation.

A more comprehensive study for the cure of 98% pure TGDDM with DDS was carried out earlier by Hagnauer and Pearce using GPC.<sup>56</sup> Their results for the cure of TGDDM with 25 wt% DDS at 177°C are similar to those of Apicella *et al.* from HPLC except that the more detailed results allowed kinetic analysis to be carried out. They noted that over the first 20% of cure the depletion of TGDDM occurred in parallel to the disappearance of DDS, supporting the proposition that the primary amine–epoxy addition reaction dominates the early stages of cure. By varying the stoichiometry and measuring the initial rates from the GPC conversion data, they showed that the initial reaction was first order with respect to TGDDM and second order with respect to DDS as shown in eq. 10.

$$-d[\text{TGDDM}]/dt = k[\text{TGDDM}][\text{DDS}]^2 \quad (10)$$

This is in agreement with Rozenberg's finding<sup>15</sup> that if there are no other species present that are capable of catalyzing the epoxy-amine addition reaction, then primary amine groups can act as the catalyst. Their GPC results also suggested that the secondary amine reaction was much slower than the primary amine reactions.

#### 4.3. Nuclear magnetic resonance spectroscopy during network formation

The advent of <sup>13</sup>C solid phase, cross polarization (CP), magic angle spinning (MAS) NMR<sup>52</sup> has enabled the study of network development beyond the gel point for the cure of TGDDM/DDS resins.<sup>34,58-61</sup> One of the difficulties with solid state NMR is that as the mobility of structural units is decreased and packing increases, the relaxation times increase, resulting in increased peak widths. In a highly crosslinked material this leads to severe peak overlap and often makes resolution of peaks for carbon atoms in similar environments an intractable problem.<sup>57</sup> To overcome this uncertainty, it is necessary to have a good knowledge of peak positions from solution NMR spectra of model compounds. It is also critical that one can accurately predict which types of structural units are likely to be present and the expected degree of line broadening.<sup>57</sup>

As highlighted in Section 2, Attias and co-workers carried out a series of detailed studies on model compounds to identify the possible structural units from the reaction of *N,N*-diglycidylanilino groups with aromatic amines. Using the knowledge gained from this research, Attias, Block and Laupretre<sup>58,59</sup> employed <sup>13</sup>C CP/MAS NMR to characterize fully cured TGDDM/DDS networks, as well as samples of TGDDM cured with the more reactive DDM. They made an assumption that no intermolecular etherification occurred, citing the results of their model studies. This meant that the structural features which they considered were present in cured samples were the products of amine-addition reactions and intramolecular cyclizations as discussed in Section 2.

The aliphatic part of the spectrum was then decomposed into elementary resonances by simulating the spectral shape as the sum of Lorentzian lines generated by computer. The areas of the simulated peaks then yielded values for the concentration of the various structural features. Figure 3 is a reproduction of such a simulation for a partially cured (90 min at 150°C) sample of stoichiometric TGDDM/DDS.<sup>58</sup> Considering the fact that line broadening is even greater in a fully cured sample, their estimation of 10% uncertainty associated with the simulation technique seems somewhat conservative. A basic comparison was made between the total number of epoxy groups reacted as calculated by the simulations and as determined using FTIR to measure the changes in the infrared epoxy band. The comparison showed no large discrepancies. However, they were on average only able to account for 90% of the original epoxy groups using their simulation method.

Results were reported for TGDDM with 26 wt% and 37 wt% DDS (i.e. excess epoxide and stoichiometric respectively) cured at 180°C for 6 hours and TGDDM with 22 wt% and 32 wt% DDM cured at 180°C for 4 hours. For TGDDM with 37% DDS, it was found that 20% of the epoxy groups were consumed in the formation of ether groups, all of which were assumed to be cyclic; 10% formed 1,2,3,4-tetrahydro-3-hydroxyquinoline units; reaction of only 25% of the secondary amine groups produced by the primary amine-epoxy addition reaction (which was complete), with three quarters of these occurring intramolecularly; and 5% of the initial epoxy groups remained unreacted. Similar results were obtained for the 26 wt% DDS sample,



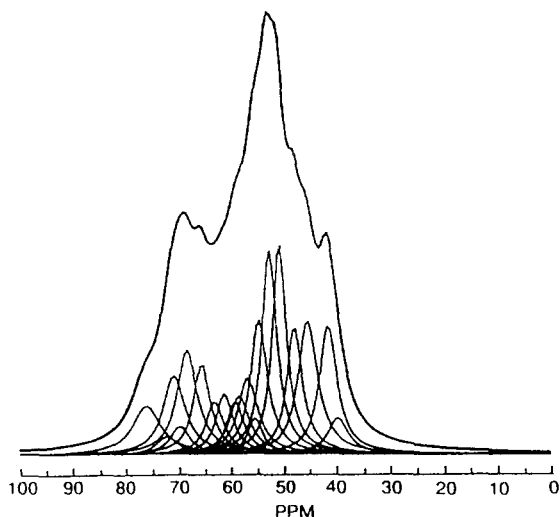


FIG. 3. Simulation of a solid state  $^{13}\text{C}$  NMR spectrum taking account of individual structural features for a partially cured TGDDM/DDS sample (reproduced from ref. 58).

though with slightly more secondary amine reaction and more unreacted epoxy groups. The samples cured with the more reactive DDM showed greater secondary amine reaction at about 65% and only half of these reactions resulted in rings for both stoichiometries. As a consequence of this, etherification and the number of 1,2,3,4-tetrahydro-3-hydroxyquinoline groups produced was reduced.

Attias *et al.* thus concluded that the network structure of cured TGDDM/DDS contained a large number of small cyclic structures and thus has a considerably lower crosslink density than might otherwise be expected for a system with such high functionality.

A similar study to that of Attias *et al.* was undertaken by Grenier-Loustalot and co-workers<sup>34,60</sup> except that they only resolved the aliphatic carbon peak into primary and secondary alcohol, ether and epoxy peaks. The amine functionalities were then determined by chemical balances. Several commercial TGDDM resins, as well as a purified form of TGDDM, were cured with a stoichiometric amount of DDS. They also found for TGDDM and MY721 that about 20% of the epoxy groups formed ethers when cured at temperatures up to 185°C. However, another commercial TGDDM resin (LOPOX 3302 from DCF Chimie) showed significantly more etherification with up to 45% of consumed epoxy groups forming ethers. A correlation between the final glass transition temperature ( $T_g$ ) of samples with the percent of ether groups and the percent of hydroxyl groups (i.e. degree of amine addition) showed that increased amine reaction resulted in higher  $T_g$ s while increasing levels of etherification yielded lower  $T_g$ s.

Mertzel *et al.*<sup>61</sup> carried out a more qualitative study using solid state  $^{13}\text{C}$  CP/MAS NMR to investigate the degree of ether cyclization in cured TGDDM/DDS matrices. They observed that in a sample with an initial excess of epoxide (20 wt% DDS) there was evidence for considerable intermolecular etherification, while in a sample with a slight initial excess of DDS (40 wt% DDS), most ether groups appeared to be involved in small cycles. This was rationalized as showing that with a higher concentration of epoxy present, the hydroxyl groups formed by the reaction of amines have more epoxy

functionalities in their environment that compete with the intramolecular hydroxyl-epoxy reaction.

These results contradict the assumption made by Attias and his co-workers that no intermolecular etherification reactions occur in the cure of TGDDM/DDS, and leaves this issue somewhat unresolved. One clear point from all of the NMR studies is that etherification reactions are significant in the cure of TGDDM/DDS resins. It is worth noting that this is different from what was observed for the cure of DGEBA/DDS by Grenier-Loustalot *et al.*<sup>62</sup> which showed negligible etherification even at the end of the cure reaction. Also Grenier-Loustalot *et al.*<sup>34</sup> later found that catalyzed TGDDM/DDS cure (i.e. with  $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$  and *N,N*-dimethylbenzylamine) resulted in a much greater degree of etherification reactions via the mechanisms described in Section 2, and thus was more likely to be intermolecular.

Mertzel and co-workers focused most of their NMR studies on the application of the  $^{13}\text{C}$  dipolar dephasing experiment.<sup>61</sup> Using this technique on the quaternary phenyl carbon with nitrogen attached, they were able to distinguish between the unprotonated tertiary amine (junction point) and the influence of the more mobile secondary amine hydrogens. If it was assumed that in a cured sample all primary amines had reacted (a reasonable assumption based on other studies) then the percentage of junction points could be determined. Data obtained in this way for TGDDM/DDS samples were compared with a network model that they had developed<sup>63</sup> and used to calculate the molecular weight between crosslinks ( $M_c$ ) for three different stoichiometries. Their results showed that as the DDS concentration decreased,  $M_c$  decreased. In other words, the greater excess of epoxy functionalities led to a higher crosslink density. This was interpreted as reflecting an increase in the degree of secondary amine reaction and an increase in the number of effective ether crosslinks (i.e. intermolecular). This is in agreement with the observation of Attias *et al.* that the highest crosslink density for a TGDDM/DDS system is obtained if epoxy functionalities are in excess.

NMR studies have thus already provided valuable insight into the development of network structure in TGDDM/DDS systems and, in the future, may be expected to yield additional information. The results at present, though, are limited by the uncertainty inherent in solid state techniques. Moreover, mechanistic information can only be inferred from final concentrations as the methods do not lend themselves to real-time measurement during cure.

#### 4.4. Vibrational spectroscopy of curing TGDDM/DDS

The most comprehensive study using mid-IR spectroscopy for the cure of TGDDM/DDS resins was by Morgan and Mones.<sup>7</sup> This involved recording the spectra of samples previously cured between sodium chloride plates. A measure of changes in epoxy, primary and secondary amine, ether and hydroxyl group concentrations was made using the relevant absorption bands. It was found that at 177°C, the dominant reaction during cure was primary amine-epoxy addition and that this was an order of magnitude faster than both secondary amine addition and etherification. Between 177 and 300°C, the TGDDM/DDS resins were found to undergo complex degradation reactions involving dehydration, oxidation and the decomposition of etherification reaction products which, it was suggested, resulted in the formation of propenal.<sup>7</sup>

Moacanin *et al.*<sup>64</sup> studied the cure of TGDDM/DDS also, though they only monitored hydroxyl, epoxy and primary amine bands. They compared their results with DSC measurements on a similar sample at the same temperature in a separate experiment and concluded that the DSC conversion data paralleled the primary amine consumption and not the epoxy consumption. Few data points were taken so only a basic kinetic analysis of the cure was possible.

The major difficulties in obtaining quality data from mid infrared spectra includes: (1) the necessity to utilize a reference band if several samples are used in the analysis; (2) the small sample thickness that has to be used ( $\approx 10 \mu\text{m}$ ) and (3) the limited substrates one can employ for preparing samples. Recently, the quality of data reported for thermal curing studies using mid infrared spectroscopy has improved considerably for other epoxy-amine systems.<sup>65</sup> However, no new detailed studies for the cure of TGDDM/DDS have been published.

The complimentary technique to mid infrared spectroscopy, Raman spectroscopy, has been of little use in the past for studying aromatic epoxy-amine systems owing to the strong fluorescence of these systems which obscures the Raman signal. However recent developments, including the advent of Fourier transform Raman spectroscopy (FT-Raman) operating in the near infrared region, have overcome many of the earlier limitations. Walton and Williams<sup>66</sup> carried out a preliminary study for the cure of the TGDDM resin, MY720, with DDS using FT-Raman and observed significant spectral changes during cure. By making band assignments they were able to attribute the changes to the decrease in amine and epoxy group concentrations. Recently, de Bakker *et al.*<sup>67</sup> performed a more detailed FT-Raman study for the cure of the TGDDM resin, MY721, with DDS comparing the results with those obtained for similar samples using near infrared spectroscopy. It was found that the FT-Raman technique had potential as a cure monitor. This technique revealed evidence for a back-biting reaction resulting in 1,2,3,4-tetrahydro-3-hydroxyquinoline structures probably due to chlorohydrin impurities in MY721 (Section 3.2).

The quantitative aspects of using Raman and near infrared spectroscopy to study epoxy resin cure have been recently examined for a diglycidyl ether resin<sup>68</sup> and it was confirmed that Raman spectra could be employed as reliably as near infrared for determining epoxide group concentrations although the reliability of other bands was not established.

#### 4.5. Near infrared analysis of TGDDM/DDS

NIR is particularly useful in the study of epoxy-amine systems owing to the strong overtone and combination bands observed for amines<sup>69,70</sup> and epoxides.<sup>71</sup> NIR spectroscopy was first used by Dannenberg<sup>72</sup> to determine the epoxy content of a commercial epoxy resin, EPON 828 (a DGEBA resin from Shell Chemical Company). He measured the consumption of epoxy groups during cure with the amine hardener, ethylenediamine, as well as monitoring the changes in hydroxyl bands. It was concluded that NIR spectroscopy could be used to accurately determine the epoxide and hydroxyl content of epoxy resins. More recently, Shriering *et al.*<sup>73</sup> used NIR spectroscopy to study the cure of the same epoxy resin (EPON 828) but with the hardener *meta*-phenylenediamine and obtained semi-quantitative results for the concentrations of hydroxyl and secondary amine groups in cured samples. They observed that the primary amine band completely disappeared during cure.

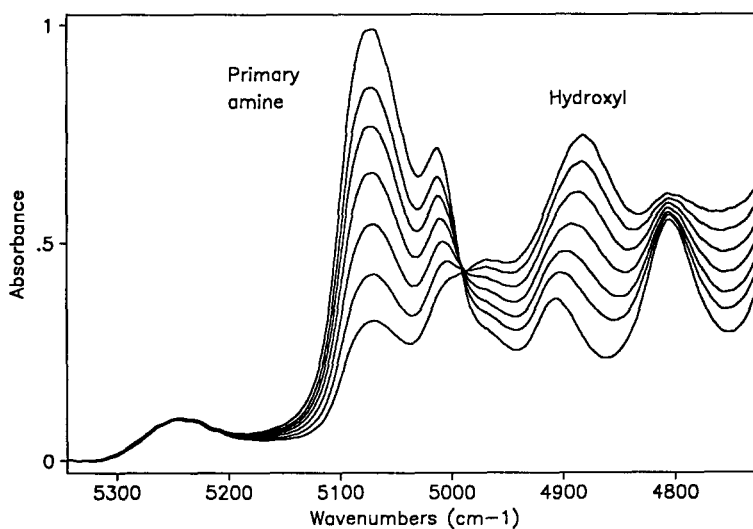


FIG. 4. NIR spectra of MY721 with 27% DDS at 160°C in the primary amine combination region (peak at 5072  $\text{cm}^{-1}$ ) recorded after heating for 2, 10, 14, 18, 22, 26 and 30 min.

NIR spectroscopic studies for the cure of TGDDM/DDS with<sup>74</sup> and without the  $\text{BF}_3 : \text{C}_2\text{H}_5\text{NH}_2$  catalyst<sup>75</sup> have been reported in order to develop a fibre optic cure monitoring technique for composite fabrication. It was demonstrated that using 600  $\mu\text{m}$  silica optical fibres, quality spectra were obtainable over most of the NIR region for samples remote from the FTIR spectrometer which had been set-up for NIR operation. Some spectral artefacts due to the cladding used on the optical fibres were identified.<sup>75</sup> The consumption of primary amine groups was found to be easily measured and epoxy and hydroxyl bands were also monitored. Figure 4 shows successive NIR spectra in the primary amine and hydroxyl combination band region during the reaction of TGDDM with DDS. The decrease in amine and increase in hydroxyl with time may be seen. The presence of an isosbestic point near 5000  $\text{cm}^{-1}$  was taken as an indication that Beer's law was obeyed and the spectra could be used for obtaining absolute concentrations of functional groups. These studies clearly demonstrated the potential for NIR spectroscopy to be employed as a real time *in situ* cure monitor while also highlighting the potential for more detailed analysis of the NIR spectra to provide greater information on the cure of TGDDM/DDS resins.

The advantages of carrying out a systematic investigation of the near-infrared region have been recently demonstrated in studies for the cure of diglycidyl ether<sup>76</sup> and diglycidyl amine<sup>77</sup> epoxy resins with DDS as full concentration profiles of primary, secondary and tertiary amine, ether, hydroxyl and epoxide were obtained over the entire cure cycle. Figures 5(a) and (b) show the changes in concentration of amine groups for the cure of TGDDM (the commercial resin, MY721) with DDS at 160°C.<sup>77</sup> The large number of data points obtainable by using rapid-scanning FT-IR spectroscopy means that accurate empirical reaction rate curves may be generated for comparison with the theoretical models, such as those developed by Chiao<sup>46</sup> and Cole<sup>43,47</sup> to rationalize the DSC data (eqs 7 and 8, respectively, of Section 4.1). Unlike a DSC analysis, no assumptions regarding the relative rates of primary and secondary amine reaction with epoxide were necessary and it was possible to

determine the absolute reaction rates and thus rate coefficients which gave the best fit to the data for an assumed reaction mechanism. For MY721 cured at 160°C with 27% DDS (an excess of epoxy resin over amine) it was found that the reaction was autocatalytic in hydroxyl groups formed by the ring opening of the epoxide. The secondary amine reaction rate was found to be slower than that for the primary amine and a substitution effect ( $k_2/k_1 = 0.215$ ) was clearly demonstrated. This may arise from steric effects on the N–H group once the primary amine has reacted. This result indicates the limitations of those DSC analyses in which assumptions of equal reactivity of primary and secondary amines with the diglycidyl amine epoxy groups were made.<sup>43,47</sup> An important consequence of the lower secondary amine reactivity is that, in the ‘fully cured’ resin, there will be a high level of unreacted secondary amine which may adversely affect its environmental performance and mechanical properties.<sup>52</sup>

While NIR spectroscopy can only measure those functional groups which show high spectral anharmonicity due to the presence of a light atom (e.g. N–H, C–H, O–H) it was found that processes such as etherification could be determined by the observation of an excess epoxide consumption over that from amine group reactions.<sup>77</sup> Two mechanisms were observed for this epoxy–hydroxyl reaction – a direct second order reaction and one catalyzed by the tertiary amine groups produced by secondary amine–epoxy reaction. The overall reaction rates at 160°C were given by eqs 11–15:

$$-d[\text{PA}]/dt = 3.3 \times 10^{-4}[\text{PA}]^2[\text{EP}] + 6.75 \times 10^{-3}[\text{PA}][\text{EP}][\text{OH}] \quad (11)$$

$$-d[\text{SA}]/dt = d[\text{PA}]/dt - 1.45 \times 10^{-3}[\text{SA}][\text{EP}][\text{OH}] \quad (12)$$

$$-d[\text{TA}]/dt = 1.45 \times 10^{-3}[\text{SA}][\text{EP}][\text{OH}] \quad (13)$$

$$-d[\text{ET}]/dt = 6.0 \times 10^{-4}[\text{EP}][\text{OH}] + 9.0 \times 10^{-4}[\text{EP}][\text{OH}][\text{TA}] \quad (14)$$

$$-d[\text{EP}]/dt = d[\text{TA}]/dt + d[\text{ET}]/dt - d[\text{PA}]/dt \quad (15)$$

These rate equations are based on kinetics which are not diffusion controlled and would therefore be expected to apply only up to the gel point of the resin. However, the experimentally determined rate curves (obtained as the derivative of the concentration–time curves Figs 5(a) and (b)) will also reflect the chemorheological changes during the crosslinking reaction. The primary amine reactions are insensitive to the developing network since they are more reactive than the secondary amine and are almost totally consumed prior to gelation in a linear polymerization reaction.<sup>2</sup> In contrast, it has been found by examining the NIR results in conjunction with dynamic mechanical analysis (DMA) for the cure of TGDDM/DDS,<sup>77</sup> that the secondary amine–epoxy reaction rate coefficient (eq. 13) after gelation was sensitive to the developing network. This is shown in Fig. 6 in which the reaction rate data are superimposed on a phase diagram obtained from DMA data described later in Section 4.7 (Fig. 8). It is noted that the rapid decrease in reactivity occurs at the onset of gelation and at the onset of vitrification. Reaction continues into the glassy state, but at a decreasing rate. Etherification reactions between hydroxyl and epoxy groups also continue as the network develops but are reported to be less sensitive to gelation<sup>77</sup> possibly due to the ease of intramolecular reactions to form the morpholine ring, structure **11** (Section 2).

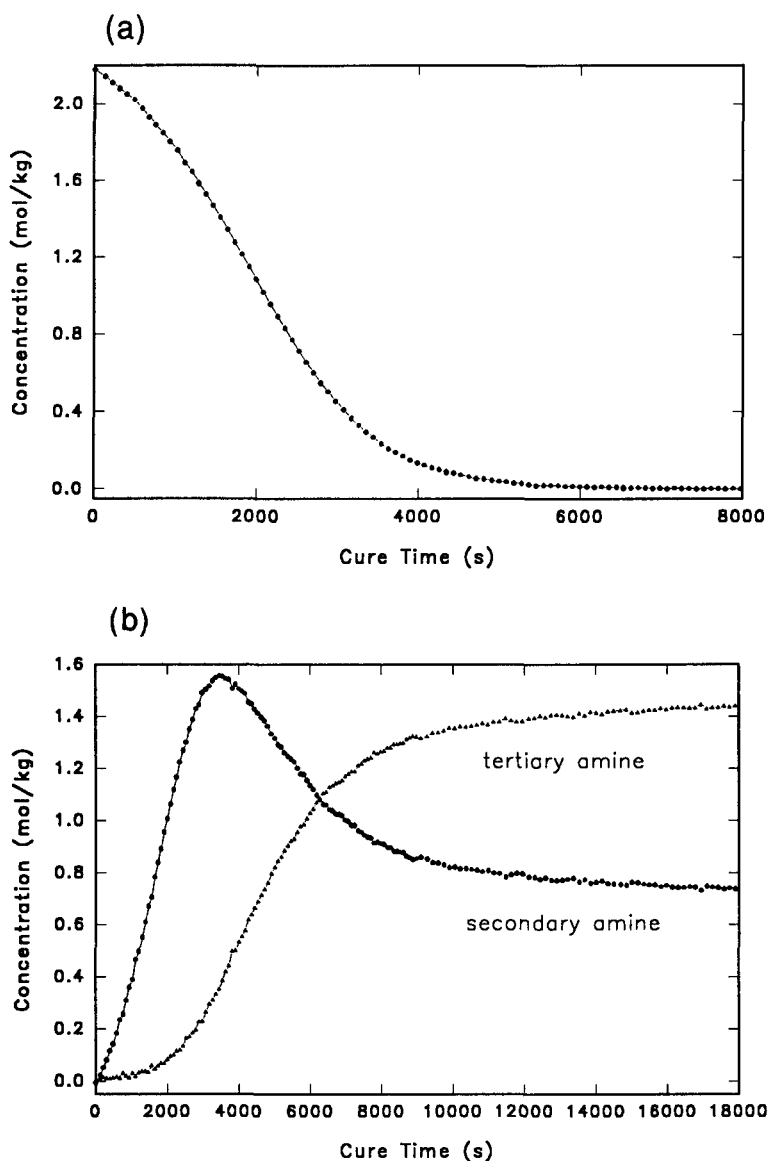


FIG. 5. Plots of absolute group concentration obtained from the NIR spectra of MY721 with 27% DDS at 160°C as a function of time of cure; (a) primary amine (b) secondary and tertiary amine.

#### 4.6. Simultaneous DSC-FT-IR analysis of cure

NIR analysis of the cure of TGDDM/DDS has enabled kinetic details to be examined. When these results were compared with those from DSC, it was found that there were limitations to the assumptions inherent in both isothermal and scanning DSC experiments.<sup>53,77</sup> Simultaneous analysis by FT-IR and DSC has recently been developed in the mid IR region<sup>78,79</sup> and applied to the study of the cure of epoxy resins by using reflectance to minimize the problem of high infrared absorptivity of the resin at path lengths consistent with an adequate DSC signal.<sup>80</sup> This fundamental problem was overcome by working in the NIR region where absorptivity is lower by two orders of magnitude so that path lengths of 1 mm may be used on samples

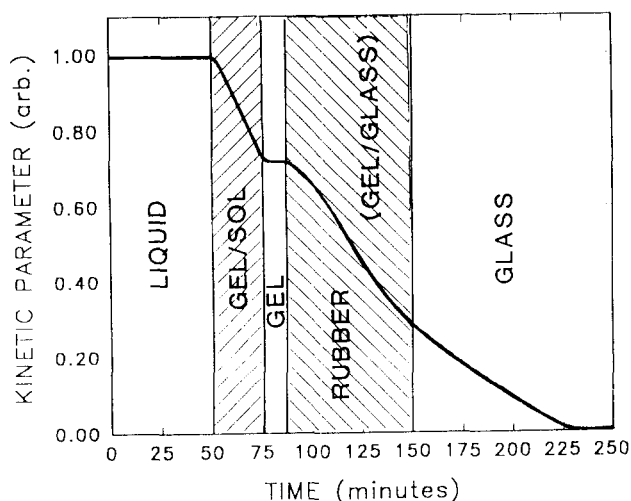


FIG. 6. Schematic diagram for change in the secondary amine-epoxy rate parameter during network formation by MY721 with 27% DDS at 160°C.

of 10 mg, which is ideal for DSC analysis.<sup>49</sup> The analytical method described in Section 4.5 was used to determine absolute concentrations of primary, secondary and tertiary amine, epoxy, hydroxyl and ether groups from which instantaneous reaction rate curves were calculated for the cure of TGDDM with DDS at temperatures of 150°C and 170°C. By using these rates along with the heat flow data obtained from the sample at the same time, the reaction enthalpies for the TGDDM epoxy groups reacting with primary amine, secondary amine and hydroxyl were calculated and reported to be  $-83$ ,  $-131$  and  $-65 \text{ kJ mol}^{-1}$  respectively.<sup>49</sup> This is significant as most kinetic analyses of resin cure by DSC have assumed equal reaction enthalpies. The error in the analysis is only significant when a detailed kinetic scheme – such as eqs 7 and 8 (Section 4.1) – is used to analyse the DSC curve. An average enthalpy of reaction for epoxide of  $-92 \pm 1 \text{ kJ mol}^{-1}$  was calculated from isothermal DSC and the NIR epoxide conversion data. This was lower than the value of  $-105 \text{ kJ mol}^{-1}$  from dynamic DSC results<sup>8</sup> suggesting that exothermic reactions other than amine-epoxy reaction have occurred at the high temperatures reached in a scanning experiment. This leads to an overall under-estimation of the extent of reaction.<sup>49</sup>

The simultaneous method also allowed the 'true' DSC baseline to be determined since the effect of the change in heat capacity of TGDDM/DDS on vitrification appeared as an anomaly in the heat flow compared to the absolute reaction rate of the resin.<sup>49</sup> This has also been observed by using 'modulated' DSC in which the reversible and non-reversible heat flow in the curing resin system were separated.<sup>81</sup>

#### 4.7. Chemorheology of TGDDM/DDS

It was noted in Section 4.5 that the secondary amine-epoxy reaction was sensitive to network development and that the balance of intermolecular and intramolecular reactions of amine and hydroxyl groups with adjacent epoxide will be influenced by the mobility of the functional groups. The study of the chemorheology of epoxy resins requires dynamic mechanical analysis over a wide viscosity range and this has been achieved either by using a fluids spectrometer followed by a mechanical spectrometer

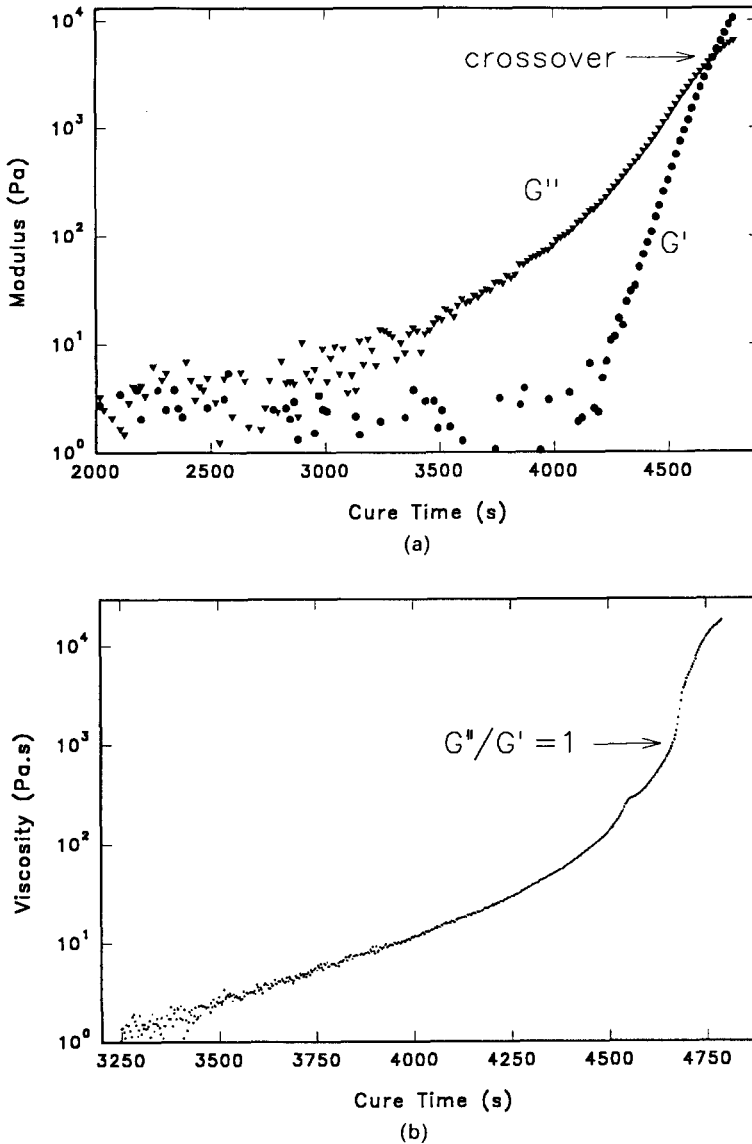


FIG. 7. (a) Change in storage ( $G'$ ) and loss ( $G''$ ) modulus during cure of MY721 with 27% DDS at 160°C up to the gel point (the crossover). (b) Change in shear viscosity with time of cure for MY721 with 27% DDS at 160°C.

or by supporting the resins on a glass braid as in Torsional Braid Analysis, pioneered by Gillham.<sup>9</sup>

In the processing of epoxy resins, the most important rheological property is the time to gelation. The dynamic mechanical properties of storage modulus  $G'$ , loss modulus  $G''$  and loss tangent ( $\tan \delta$ )  $G''/G'$  are used to characterize the rheological changes, and it has been proposed by several researchers<sup>82-84</sup> that the crossover point between  $G'$  and  $G''$  (i.e.  $\tan \delta = 1$ ) occurs at the gel point of crosslinked systems. However this has remained a contentious issue for many cases and Winter<sup>82</sup> concluded that the crossover point can only be used as a measure if the point is independent of the measurement frequency used. Recently, Lairez *et al.*<sup>83</sup> studied the rheological behaviour of an epoxy-amine system (DGEBA/DDS) near its gel



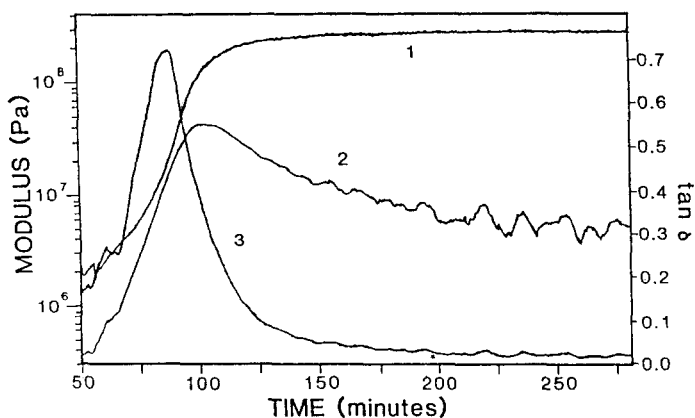


FIG. 8. Plots of (1) storage modulus,  $G'$  (2) loss modulus,  $G''$  (3)  $\tan \delta$  vs cure time after gelation as measured by DMA for MY721 with 27% DDS at 160°C.

point and found that the crossover point did vary slightly with the measurement frequency used. The observed change was from 61 to 63 min with a change of frequency of 0.1 to 10 Hz. An error of this magnitude is probably less than that expected from temperature variations that could occur during the cure. Tung and Dynes<sup>84</sup> found that agreement between the crossover point and gel points measured using the ASTM gel time test (i.e. slow stirring with a stick until an elastomer with a memory forms) was best with a test frequency of 10  $\text{rad} \cdot \text{s}^{-1}$  and a cure temperature at least 30°C above the glass transition temperature at gelation.

Figure 7(a) shows the change in storage and loss moduli at 10  $\text{rad} \cdot \text{s}^{-1}$  during the isothermal cure of MY721 with 27% DDS at 160°C. In Fig. 7(b) the shear viscosity of the same sample is plotted and it may be seen that the crossover point ( $G''/G'$ ) in Fig. 7(a) corresponds to a viscosity of about 10<sup>3</sup> Pa · s, which is the point of sharpest increase in viscosity. A viscosity of 10<sup>3</sup> Pa · s is often taken as indicative of gel formation<sup>84</sup> and the close agreement with the time at which  $G''/G' = 1$  indicates that an unambiguous gel point may be defined for TGDDM/DDS during cure.

The development of the network beyond the gel point may be seen from the changes in the storage and loss moduli and  $\tan \delta$  shown in Fig. 8<sup>77</sup> for the same sample as shown in Figs 7(a) and 7(b). Harran and co-workers<sup>85-87</sup> have also studied the changes in dynamic mechanical properties of a commercial TGDDM (LOPOX 3202 from CDF Chemie) cured with DDS at 180°C, using sinusoidal shear. From Fig. 8 it is seen that the characteristic features of the changes in the dynamic mechanical properties include a steady increase in the storage modulus that is arrested fairly quickly after a particular time; a steady increase in the loss modulus till a point is reached where retardation of the increase results in a maximum after which the value of  $G''$  decreases at an ever slower rate; and a sharp rise in the  $\tan \delta$  value to a maximum after which the value drops quickly to nearly zero.

The behaviour of the storage modulus is what would be expected as the crosslinking reactions increase the complexity of the network, and thus the modulus, until vitrification freezes out the cure reactions. The changes in the loss modulus are more interesting and Harran *et al.*<sup>85,87</sup> have interpreted the maximum that occurs in  $G''$  as representing the onset of vitrification. After the onset of vitrification, the storage modulus continues to rise, though at an ever slower rate, reflecting continuing

reaction. No change in  $G'$  is observed after about 200 min cure which is consistent with the results for the changes in the functional group concentrations in Fig. 5(b) during cure which show no significant reaction of secondary amine groups after this time. However, etherification reactions persist beyond this point showing that they have little effect on the storage modulus of the sample, though the loss modulus appears to continue to decrease.

The peak in the  $\tan \delta$  curve has not been attributed any particular significance<sup>77,85</sup> as it is probably the result of several different ill-defined influences including the incorporation of remaining sol into the gel network. Thus the DMA results provide valuable insight into the changing system morphology as cure proceeds to completion.

## 5. THE EFFECT OF IMPURITIES ON RESIN CURE KINETICS

Studies of resins of different commercial origin<sup>5,77,85</sup> have shown that there are considerable differences in the rheological properties with time of cure and this may be attributed to the impurities from synthesis as described in Section 3.2. For example, the resin MY720 consists of only 63% TGDDM and, as shown in the chromatographs in Fig. 2, contains both polar impurities and oligomers. The nature of these impurities depends on the synthetic route. Resin MY721, which has a higher TGDDM content (79%), also contains chlorohydrin impurities, species **18** of Section 3.2. At the high temperatures involved in resin cure (e.g. 177°C), the chlorohydrin groups have been shown to undergo an intramolecular cyclization reaction to produce species **21**. Such reactions have been followed by MIR<sup>77</sup> and FT-Raman<sup>67</sup> and must be clearly elucidated as spectral interferences may occur when quantitative functional group analysis is performed.<sup>77</sup> This reaction also liberates hydrogen chloride which might catalyze the epoxy ring-opening reaction.

The reaction of TGDDM with both primary and secondary amine groups of DDS has been shown to be catalyzed by hydroxyl groups via a mechanism such as that shown in Scheme 4 or 5 of Section 2. Consequently it would be expected that oligomers (which have hydroxyl groups due to ring-opening of epoxide) and the impurities identified in commercial TGDDM resins as containing hydroxyl groups (e.g. compounds **18–22** in Section 3.2) would catalyze the curing reaction leading to a gel-time shorter than that for the purified resin. This may be the principal reason for the differences in reaction mechanism deduced from kinetic analyses of commercial resins. In a recent study, three different samples of TGDDM were characterized by FT-IR to determine hydroxyl content<sup>5</sup> and the effect on the gel-time was determined. Figure 9(a) shows the spectra obtained and Fig. 9(b) the assignment of the spectrum to three components for one of the resins:

- Peak 1: Free hydroxyl such as the secondary alcohol group in compound **21**;
- Peak 2: Intramolecularly hydrogen bonded glycols and hydroxyls adjacent to amines or epoxides;
- Peak 3: Hydroxyls hydrogen bonded to several groups through both oxygen and hydrogen to give 'polymeric' species. (This may be complicated by the presence of an N–H stretch at this frequency if any impurity such as **17** were present.)

It might be expected that only the hydrogen bonded species (Peaks 2 and 3) would have a catalytic effect on the cure reaction. This was confirmed by a study of the

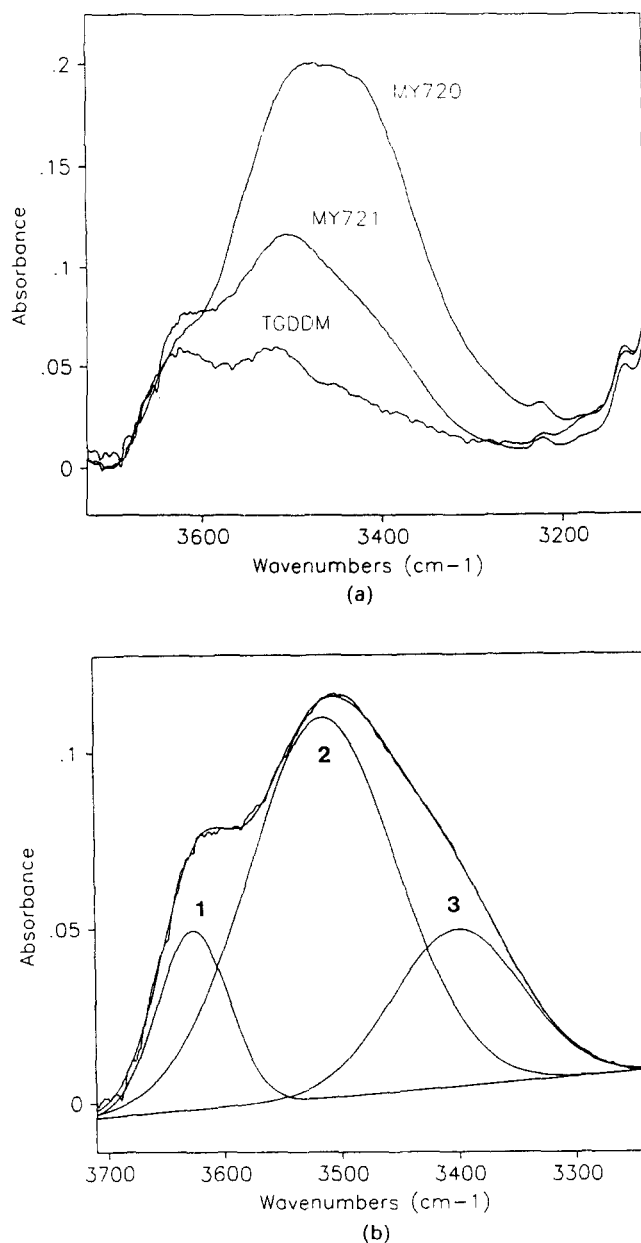


FIG. 9. (a) Infrared spectra for MY720, MY721 and purified TGDDM in the hydroxyl stretching region. (b) Curve fitting of three peaks for the cure for MY721 above, for hydroxyl groups in different environments.

primary amine consumption rate for the three resins and analysis of the cure kinetics according to eq. 11.<sup>5</sup> The initial hydroxyl group concentration which produced the observed amine group concentration profile up to gelation was consistent with the concentration of hydrogen bonded hydroxyl groups given from the curve fitting of Fig. 9 as described above. The conclusion from these studies was that there should be a marked effect on the observed gel times for the three resins. The gel times (determined as  $G''/G' = 1$ ), the calculated functional group concentrations from eqs 11–15, and as the epoxide conversion at gelation are given in Table 2.

TABLE 2. Results at gel time for resins cured with 27% DDS at 160°

Resin	Calculated concentrations at gel (mol kh <sup>-1</sup> )						$\alpha_{gel}$	Gel time (min)
	1° amine	2° amine	3° amine	Ether	Epoxy	Hydroxyl		
MY720	0.115	1.36	0.708	0.357	2.67	3.15	0.54	59
MY721	0.032	1.11	1.04	0.604	2.85	3.30	0.57	78
TGDDM	0.021	1.03	1.13	0.701	2.85	3.30	0.58	90

Table 2 shows that in addition to the kinetic effect of the hydroxyl impurities, the gel time of the impure resin MY720 will be lowered also by the lower epoxy conversion ( $\alpha_{gel}$ ) required to reach the gel point. This may reflect the high oligomer content of MY720 (as shown in the chromatogram, Fig. 2) which effectively represents an initial degree of cure.

Overall, a high extent of cure is required in TGDDM resins to achieve gelation compared to glycidyl ethers and this has been attributed<sup>5</sup> to intramolecular cyclization and to the lower reactivity of secondary amines which allows chain extension to be favoured over crosslinking in the early stages of cure. The kinetic analysis, by incorporating the catalytic effect of hydroxyl impurities, allowed an empirical relation to be developed which enabled the gel time to be predicted for TGDDM resins of known impurity concentration. The critical conversion for gelation has in the past been addressed primarily through a statistical analysis of network formation.

## 6. STATISTICAL MODELLING

Theoretical approaches which model the formation of networks have found greater application in the field of thermosets in the past due to the absence of suitable analytical methods of characterization for network polymers. Though this problem has subsided somewhat in recent years owing to the great advances in technology that have occurred, for example, in NMR and infrared techniques described above, the use of mathematical models still has the benefit of being able to estimate properties that would otherwise need to be measured.

The early foundations for network theory were laid by the work of Flory<sup>88</sup> and Stockmayer<sup>89,90</sup> who proposed methods for calculating molecular weight distributions for finite molecules during a step-wise polymerization. A critical condition for the onset of gelation was developed by Flory using the theory of expectation<sup>88</sup> and Stockmayer using the derived number average molecular weights.<sup>90</sup> These approaches provide reasonable results for simple systems but quickly become very cumbersome when it is attempted to incorporate features such as unequal reactivities and intramolecular cyclizations.<sup>91</sup>

Gordon<sup>92</sup> recognized the utility of Good's stochastic theory of cascade processes for the problem of a developing network and used the approach of developing probability generating functions which allowed calculations of distributions of molecular weights and branch points in a network. This approach, sometimes referred to as 'branching theory', has been developed over the years and has been reviewed recently by Rolfe and Septo.<sup>93</sup> Dusek,<sup>94</sup> and also more recently Tsou and Peppas,<sup>95</sup> have used this extensively to model the development of epoxy-amine networks and to show the

consequences of a substitution effect on secondary amine reactivity and etherification reactions to a developing network structure.

A different approach to statistical modelling of network development was taken by Miller and Macosko<sup>96,97</sup> which used Expectation Theory to calculate average properties for non-linear systems. This recursive approach is much simpler than branching theory and provides general solutions similar to those of Flory and Stockmayer. Bokare and Ghandi<sup>98</sup> have applied this approach to the problem of epoxy-amine cure and developed a relationship that includes the effects of etherification reactions. Macosko and Gupta<sup>99</sup> recently proposed a modification of the use of Expectation Theory methods for modelling network development in epoxy-amine systems. Unfortunately, this type of approach leads to complex relationships that require substantial assumptions to obtain solutions when all the features of a real epoxy-amine cure are incorporated.

All of these methods have been hampered in the past when applied to epoxy-amine systems by a lack of good empirical data on the cure process and so have generally relied on simplified kinetic schemes, focusing on modelling the general effect of different kinetic influences on the formation of networks. This has also partly been due to the difficulty in deriving solutions using more complex kinetic relationships that fully reflect the cure of a system such as TGDDM/DDS. The ability of modern analytical methods to provide real-time concentration profiles to test the kinetic models provides an alternative approach to problems as complex as predicting the viscosity behaviour of impure commercial resin systems during fabrication under a complex temperature program.

## 7. REACTIONS OF TGDDM IN THE ABSENCE OF AMINE

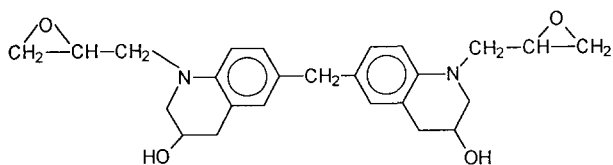
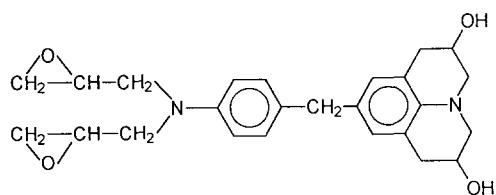
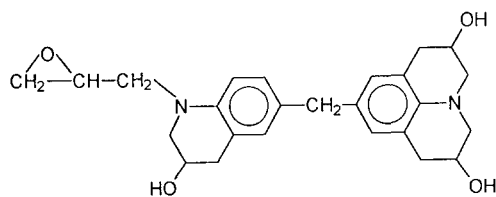
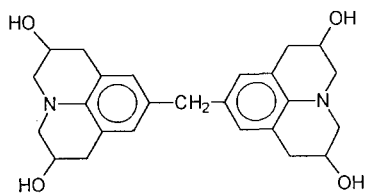
While the emphasis in this review has been on the reactions of the TGDDM epoxy resin with an amine, principally DDS, in systems which have an excess of epoxy, homopolymerization reactions may ultimately become important. This is particularly significant at higher temperatures in scanning DSC experiments when the 'residual enthalpy of reaction' is determined after an isothermal DSC experiment.<sup>38</sup> It was noted earlier (Section 4.6) that the reaction enthalpy is higher than expected for epoxy-amine reactions at these higher temperatures suggesting that homopolymerization was occurring.<sup>49,77</sup>

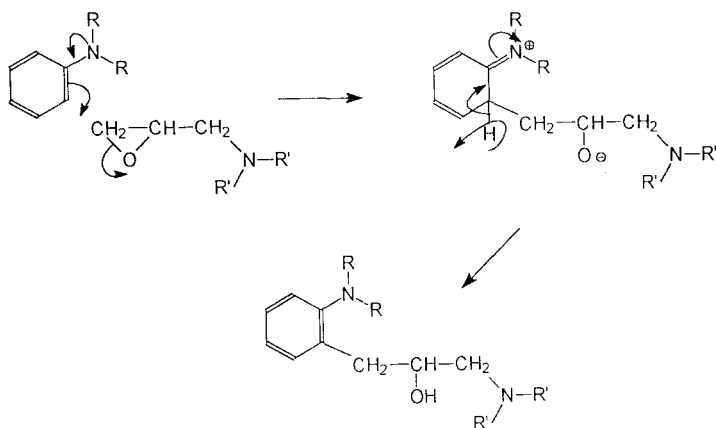
Morgan and Mones carried out a study, using Fourier transform-infrared (FT-IR) spectroscopy, of the thermal reactions of pure TGDDM, MY720 and MY720 with  $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$  catalyst.<sup>7</sup> Neat TGDDM showed negligible changes up to 177°C, while between 200 and 225°C the epoxide groups were readily consumed producing hydroxyl, carbonyl and ether groups. Above 250°C, degradation reactions dominated. Neat MY720 behaved similarly, though with slightly more reaction and fewer carbonyl groups being produced, probably due to the hydroxyl impurities. The catalyzed MY720 underwent significant reaction below 177°C with the production of ether and hydroxyl groups and above 200°C behaved similarly to the neat resins with fewer carbonyl groups being produced than in the case of the neat resins.

This is consistent with the view that the epoxy homopolymerization reaction producing ether links requires a lewis acid or tertiary amine catalyst and is not catalyzed by the tertiary amine groups on TGDDM. The epoxy reactions between 200 and 250°C were described<sup>7</sup> as possibly resulting from epoxide isomerization, oxidation

and homopolymerization reactions. It is the appearance of alternative reactions above 200°C for TGDDM that justifies limiting cure temperature profiles to below 200°C.

Costes *et al.* carried out a detailed analysis, using HPLC, FT-IR and NMR techniques, of the products from the thermal reactions of neat TGDDM and TGDDM with the tertiary amine catalyst *N,N*-dimethylbenzylamine.<sup>100</sup> It was found that for neat TGDDM at 195°C no ether groups were formed and the main isolatable products were the result of intramolecular backbiting reactions giving 1,2,3,4-tetrahydro-3-hydroxyquinoline rings. All five successive products, shown as structure **21** (Section 3.2) and structures **24–27** were identified when the reaction was carried out in refluxing 1,2-dichlorobenzene. When neat TGDDM was heated, the resin eventually gelled and led to a solid and high molecular weight product. The formation of a network structure in the absence of ether formation was rationalized by the occurrence of intermolecular reactions via a mechanism similar to the backbiting reaction (see Scheme 9, Section 2.2), as shown in Scheme 13, with an epoxy group from another molecule ‘attacking’ at the *ortho* position to the nitrogen on a TGDDM type molecule.

**24****25****26****27**



SCHEME 13.

When TGDDM was heated with 0.5% *N,N*-dimethylbenzylamine, it was observed that in addition to the products previously described for neat TGDDM, a homopolymerization reaction with the formation of ether groups occurred.<sup>100</sup> A mechanism based on a quaternary amine-alcoholate zwitterion, described previously in Scheme 7, was employed to account for the homopolymerization reaction.

These results were consistent with the earlier work of Morgan and Mones,<sup>7</sup> in that below 200°C the tertiary amine groups on TGDDM are unable to initiate the homopolymerization reaction or catalyze the etherification reaction in the same way as a Lewis acid or another tertiary amine. Costes *et al.* suggest that this is due to the steric hindrance of glycidyl groups on TGDDM and the delocalization of the lone pair of electrons on the nitrogen which manifests itself also in the reaction of epoxy groups at the *ortho* carbon on the phenyl ring.<sup>100</sup>

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