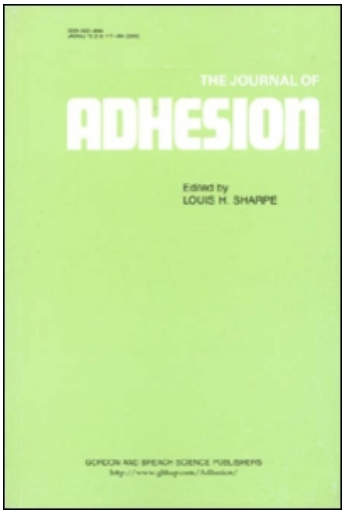

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Holubka, J. W. and Carduner, K. R.(1992) 'NMR Study of the Epoxy Crosslinking Reactions of N,N-Dimethyl-4-Chlorophenyl Urea', The Journal of Adhesion, 37: 4, 239 — 250
To link to this Article: DOI: 10.1080/00218469208033071
URL: http://dx.doi.org/10.1080/00218469208033071

J. Adhesion, 1992, Vol. 37, pp. 239–250
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Printed in the United Kingdom

NMR Study of the Epoxy Crosslinking Reactions of N,N-Dimethyl-4-Chlorophenyl Urea

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(Received April 11, 1991; in final form January 7, 1992)

The crosslinking of one-part epoxy adhesives is a complex process involving reactions of dicyandiamide and any of a variety of accelerators with epoxide functional polymers. Variations in adhesive formulation and process affect the final properties of the adhesive bond. The reactions of N,N-dimethyl-4-chlorophenyl urea, an accelerator for one-part, dicyandiamide crosslinked epoxy adhesives has been studied with Carbon-13 NMR in model systems employing phenyl glycidyl ether as the epoxy. A complex reaction mixture was observed whose composition varied with epoxy-accelerator stoichiometry and reaction temperature.

NMR peaks having chemical shifts consistent with 2-N-(4-chlorophenyl)-4-phenoxymethyl oxazolidone, a quaternary amine terminated polyether and epoxy elimination products have been observed in reaction mixtures modeling adhesive formulations. The quaternary amine terminated polyether likely results from condensation of epoxy with the dimethyl amine that is formed from N,N-dimethyl-4-chlorophenyl urea under cure conditions. Of the three products observed, only the quaternary amine terminated polyether would afford crosslinks in the actual adhesive. The other two products would consume epoxide functionality without the concurrent formation of crosslinks. The relative amounts of these three products varied as a function of reaction temperature, suggesting that variations in process conditions may affect final properties of dicyandiamide-crosslinked epoxy adhesives that are accelerated with N,N-dimethyl-4-chlorophenyl urea.

KEY WORDS NMR; epoxy crosslinking; N,N-dimethyl-4-chlorophenyl urea; oxazolidone formation; dimethyl amine formation.

INTRODUCTION

The chemistry involved in the crosslinking of epoxy resins with dicyandiamide is very complex and only partially understood. Dicyandiamide has the potential to undergo a range of transformations contributing to the complex chemistry of this adhesive system. Although adhesives incorporating this crosslinker have been used and studied for years, a thorough understanding of the cure chemistry has not been unequivocally established.[1-9] Saunders *et al.*[1] have used IR and NMR to study the tertiary-amine catalyzed dicyandiamide-epoxy crosslinking reaction and have found that polyetherification occurs at <90°C whereas addition reactions involving the

nitrile functional group of the dicyandiamide occurs at higher cure temperatures. Zahir[2] also has observed that the reaction products formed during a dicyandiamide-epoxy cure varies as a function of temperature. Similar results also were reported by Pascault *et al.*[3] with benzyldimethyl amine catalyzed dicyandiamide crosslinking reactions. DSC techniques have also been used to study the kinetics of the epoxy crosslinking reactions.[4-5] Model compound reaction studies[7] have also been used to investigate epoxy crosslinking chemistry using both IR, NMR and HPLC techniques.

The cure chemistry of one-part, dicyandiamide crosslinked epoxy adhesives is further complicated by a range of accelerators that are commonly incorporated in the adhesive formulation to control the cure response and modify the properties of the cured adhesive. A more thorough understanding of the dicyandiamide-epoxy crosslinking chemistry and effects of accelerators on the cure response can aid in better control over the process and is highly desirable as more adhesives are incorporated into automotive vehicle construction. This report will describe a mechanistic study directed toward understanding the chemistry of N,N-dimethyl-(4-chlorophenyl) urea,[10-11] a conventionally used accelerator in epoxy adhesive formulations.

EXPERIMENTAL

Materials

All materials and reagents were used without further purification. Dicyandiamide, phenyl isocyanate, N,N-dimethylbenzyl amine and phenyl glycidyl ether were obtained from Aldrich Chemical Company; the epoxy resin, Epon 828, was obtained from the Shell Chemical Company; N,N-dimethyl-(4-chlorophenyl) urea was obtained from Artel Chemical Corporation as Fikure 62U; anhydrous dimethyl amine was obtained from Matheson; DMSO-d6 was obtained from ICN Biomedicals, Inc.

NMR Spectroscopy

Solution state ^{13}C NMR spectra were acquired at a frequency of 75.5 MHz employing a Bruker MSL 300 spectrometer and associated multinuclear solution state probe. The free induction decay was averaged under conditions of broad band decoupling. No correction for NOE effects was pursued.[12] Approximately 4000 transients were averaged using a 40 deg pulse.[13] Acquisition was followed by standard Fourier transformation and phasing. Spectral referencing was to the central line of DMSO-d6 at 39.5 ppm. For some experiments, gated decoupling was used with the decoupler off during acquisition to observe scalar couplings due to directly bonded protons. In this experiment, methyl carbons are split into 4 resonances, methylene into 3, methyl and protonated aromatic carbons into 2, and non-protonated carbons are unaffected.[14] This experiment was performed to corroborate assignments made on the basis of chemical shift. Samples were prepared for NMR analysis by dissolving solid or liquid reactant or products in 3 ml DMSO-d6.

Infrared Spectroscopy

Infrared spectra were taken between two sodium chloride crystals on a Mattson Polaris FTIR spectometer using 16 scans. For solid samples, a solution of the reaction mixture was made with the appropriate solvent and the resulting material was applied to the salt crystal and allowed to evaporate at temperatures of less than 50°C for 3–5 minutes.

MODEL REACTIONS

Thermal Stability of N,N-Dimethyl-(4-chlorophenyl) Urea

A test tube containing 3.0 g N,N-dimethyl-(4-chlorophenyl) urea, *1*, was heated at 180°C for 30 minutes. The melt that resulted quickly solidified upon cooling to room temperature. The resulting solid was analyzed by ^{13}C NMR and proved to be unreacted urea. In an accompanying study, a DSC examination of *1* showed that this material has a melting point of about 130°C with an onset of decomposition of greater than 200°C and the absence of residue (product of decomposition likely to be phenyl isocyanate and dimethyl amine).

Preparation of 2-N-Phenyl-4-phenoxymethyl oxazolidone Standard

To 1.50 g (0.01 mole) of phenyl glycidyl ether in a 25 ml flask was added 1.19 g (0.01 mole) of phenyl isocyanate and about 50 mg of N,N-dimethylbenzyl amine. The reaction mixture was heated at 120°C for 60 minutes. Upon cooling to room temperature, the oxazolidone solidified to a waxy solid that was subsequently recrystallized in methanol.

Preparation of 2-N-(4-chlorophenyl)-4-phenoxymethyl oxazolidone Standard

A mixture comprising 1.0 g (1 mmol) of *1* and 1.50 g (1 mmol) of phenyl glycidyl ether was heated at 180°C for 0.5 hours. The resulting dark oil was cooled to room temperature. The oil was dissolved in about 10 ml of methanol at 40°C. The resulting solution was allowed to cool to room temperature. After sitting at room temperature for two days, a crystalline solid, *6*, separated. This solid was subsequently isolated by filtration and again recrystallized in methanol to afford a white crystalline material that was used as a standard.

Preparation of Poly(phenyl glycidyl ether)

Poly(phenyl glycidyl ether) was prepared by bubbling anhydrous dimethyl amine gas through 1.5 g (0.01 mole) of phenyl glycidyl ether at about 100–120°C. During the (approximately) 3-minute addition, the color of the reaction mixture slowly darkened and the viscosity increased. After addition of the amine, the reaction mixture was heated to 180°C for 10 minutes and then cooled to room temperature to afford a dark viscous oil.

Model Crosslinking Reactions

General Procedure A series of model crosslinking reactions were conducted by first combining the appropriate amounts (list below) of the reactants in a 1 cm diameter, 15 cm long test tube and then thoroughly mixing the contents with agitation for about one minute. The reaction mixture was then heated in an air circulating convection oven for 30 minutes, and then cooled to room temperature. The products of the reaction, generally dark oils, were dissolved in DMSO-d6 and the resulting solutions were put in an NMR tube for subsequent analysis.

Effect of Stoichiometry on the Reaction of *1* with Phenyl Glycidyl Ether

The general procedure described above was used with the molar ratio of *1* to phenyl glycidyl ether, *4*, varied in the manner summarized below:

Stoichiometry	Weight *1*	Weight *4*
6:1	1.10 g	0.15 g
1:1	0.92 g	0.75 g
1:4	0.92 g	3.00 g
1:6	0.92 g	4.50 g

Stability of Oxazolidone Under Epoxy Cure Conditions to:

Dimethylamine and Isophorone diamine a) Dimethyl amine: Gaseous dimethyl amine was bubbled through a melt of 1 g of 2-N-phenyl-4-phenoxymethyl oxazolidone melt at 180°C. After about 3 minutes the addition of the amine was stopped and the reaction mixture was heated at 180°C for an additional 15 minutes. The resulting product had infrared and NMR spectra that were identical to the starting material. b) Isophorone diamine: A mixture comprising 100 mg each of isophorone diamine and oxazolidone was heated at 180°C for 30 minutes. The resulting product was analyzed by infrared and showed no changes in the carbonyl region that would be associated with reaction of the oxazolidone.

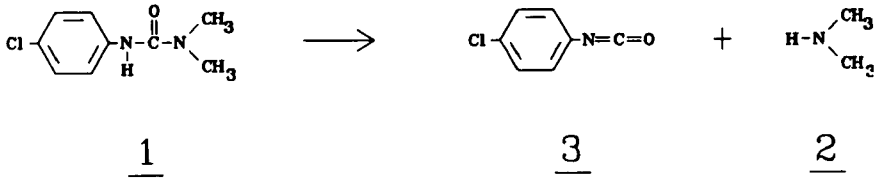
Triethanolamine 1 g 2-N-Phenyl-4-phenoxymethyl oxazolidone was added to an excess of triethanolamine and the resulting reaction mixture was heated at 180°C for 30 minutes. The resulting product was analyzed by NMR and showed no reaction of the oxazolidone.

Epoxy/Dimethylamine Reaction Product(s) A mixture comprising 1.5 g (0.01 mole) of phenyl glycidyl ether and 0.5 g (0.002 mole) 2-N-phenyl-4-phenoxymethyl oxazolidone was heated to 180°C. Gaseous dimethyl amine was bubbled through the resulting solution for about 3 minutes during which time the reaction mixture darkened and the viscosity increased. The addition of the amine was stopped and the resulting reaction mixture was heated at 180°C for an additional 15 minutes. The resulting product was a dark oil that was analyzed by infrared spectroscopy. No change in the carbonyl region was observed.

RESULTS AND DISCUSSION

Thermal Stability of N,N-Dimethyl-(4-chlorophenyl) Urea

N,N-dimethyl-(4-chlorophenyl) urea, *1*, is one of a series of accelerators that are used in one-part dicyandiamide crosslinked epoxy adhesives. The reactivity of this molecule in adhesive formulations is complex. Studies[4,6,11] have suggested that *1* accelerates the dicyandiamide-epoxide crosslinking reactions by generating, *in situ*, dimethyl amine *2*. The described work infers that *2* is formed as a result of a thermal decomposition of the urea, *1*, in a reaction that also liberates 4-chlorophenyl isocyanate *3*, (Equation 1).



1 3 2

Equation 1

Thermal decomposition reactions of this type are not without precedent. For example, similar thermal decomposition of urethanes forms the basis of the crosslinking reactions for some cathodically electrodeposited coatings. Thermal decomposition of ureas, however, has generally been found to occur at temperatures in excess of 180°C.

In the absence of epoxide, *1* was found to be unaffected by temperatures up to at least 180°C. The NMR of *1* before and after heating was identical. Differential scanning calorimetric analysis of *1* shows a melting point of about 130°C and a decomposition at 275°C (with onset of decomposition at 200°C (Figure 1)). In the

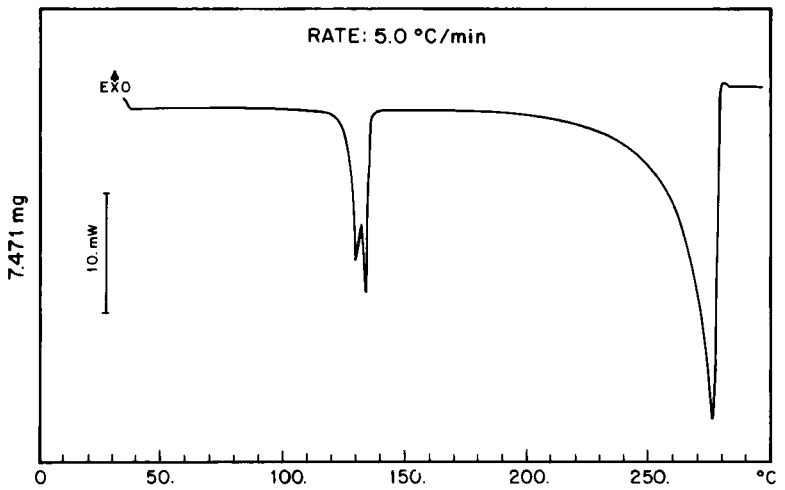
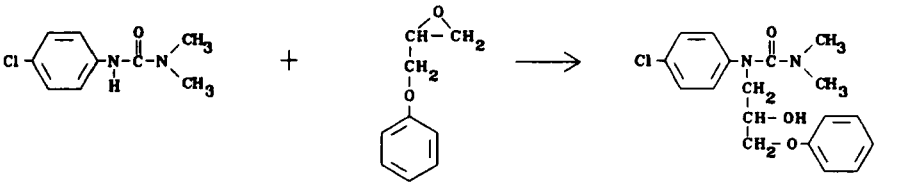


FIGURE 1 DSC scan of N,N-dimethyl-4-chlorophenyl urea.

presence of epoxide, reaction was noted at temperatures as low as 120°C, where the NMR spectrum shows a complex pattern of peaks that are unlike the starting spectrum. These observations suggest that the dimethyl amine is formed from a reaction intermediate, such as *5*, that is the condensation product of *1* with the epoxide, (Equation 2).

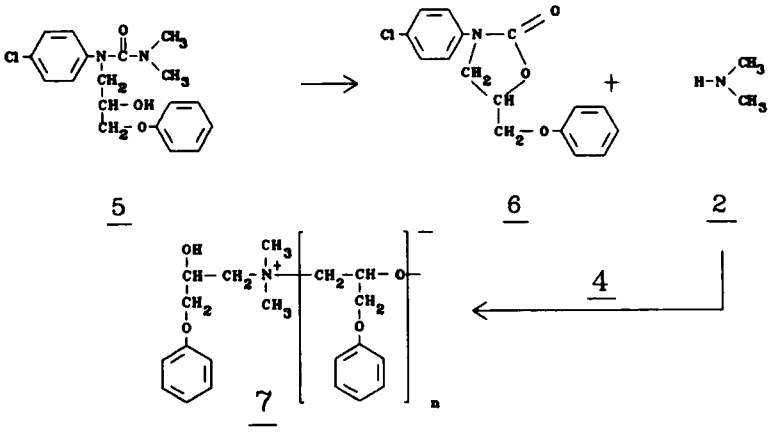


1 4 5

Equation 2

Reaction of N,N-Dimethyl-(4-chlorophenyl) Urea, 1 with Phenyl Glycidyl Ether
The most likely reaction intermediate between phenyl glycidyl ether and N,N-dimethyl-(4-chlorophenyl) urea is *5* (Equation 2). This product is formed as a result of the addition of N—H of *1* to oxirane functionality of *4*. The absence of a peak at 36 ppm corresponding to the N,N-dimethyl group (chemical shift expected to be nearly equivalent to that in *1*) strongly suggests that *5* is not present in high concentrations in the reaction mixture but, rather, is likely a transient intermediate. Direct confirmation of the presence of *5* in the reaction mixture was, thus, not unequivocally confirmed. The urea-epoxy adduct that is proposed would be expected to react further *via* either of two pathways, (Equations 3 and 4) involving intramolecular nucleophilic addition of the hydroxy group to the carbonyl group of *5*.

Along one pathway, Path A, cyclization of *5* (Equation 3) would afford oxazolidone *6* and dimethyl amine. Once formed, the dimethyl amine can add to the phenyl glycidyl ether to generate a quaternary amine that subsequently reacts with additional *4* to generate poly(phenyl glycidyl ether) *7*. Reaction along this pathway would afford one molecule of dimethyl amine (as quaternary amine in the presence of epoxy) for each oxazolidone, (Equation 3).

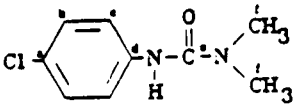
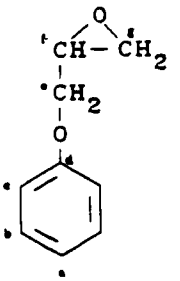
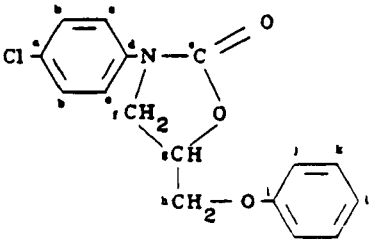
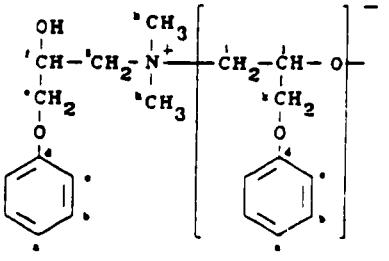


5 6 2 4 7

Equation 3

A survey spectrum of a 1:1 molar mixture of phenyl glycidyl ether:N, N-dimethyl-(4-chlorophenyl) urea reacted at 180°C for 30 minutes is shown in Figure 2. Comparison of the NMR spectrum of the reaction mixture with NMR spectra of standard compounds (Table I), indicates that unreacted *1*, oxazolidone *6*, and quaternary amine *7* are the principal compounds present in the reaction mixture. Also present in the reaction product are a multitude of minor products. Interestingly, the spectra show that the amount of oxazolidone that is formed in the reaction

TABLE I
C-13 NMR assignments for standard compounds

Assignments (ppm)	Structure
a 121.6 b 128.2 c 119.8 d 140.7 e 155.8 f 36.2	
a 120.8 b 129.5 c 114.4 d 158.3 e 68.8 f 49.7 g 43.7	
a 121.1 b 128.8 c 118.0 d 138.3 e 154.1 f 46.3 g 70.8 h 68.3 i 158.0 j 114.6 k 129.5 l 123.5	
a 120.8–120.4 b 129.4 c 114.7–115.5 d 159.0–157.6 e 67.0 f 62.4 g 71.0 h 46.0–45.8 i 71.9 (n = 1) 84.9–84.5 (n>1) j 60.3–60.1 (n = 1) 68.2 (n>1, band center) k 77.8–76.7	

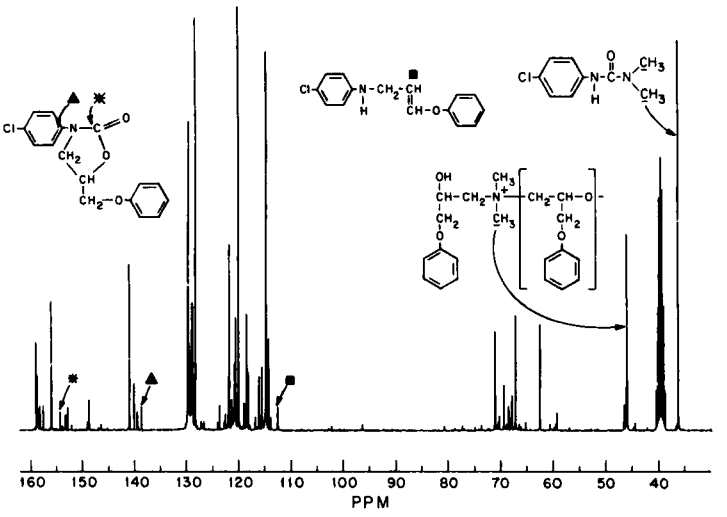
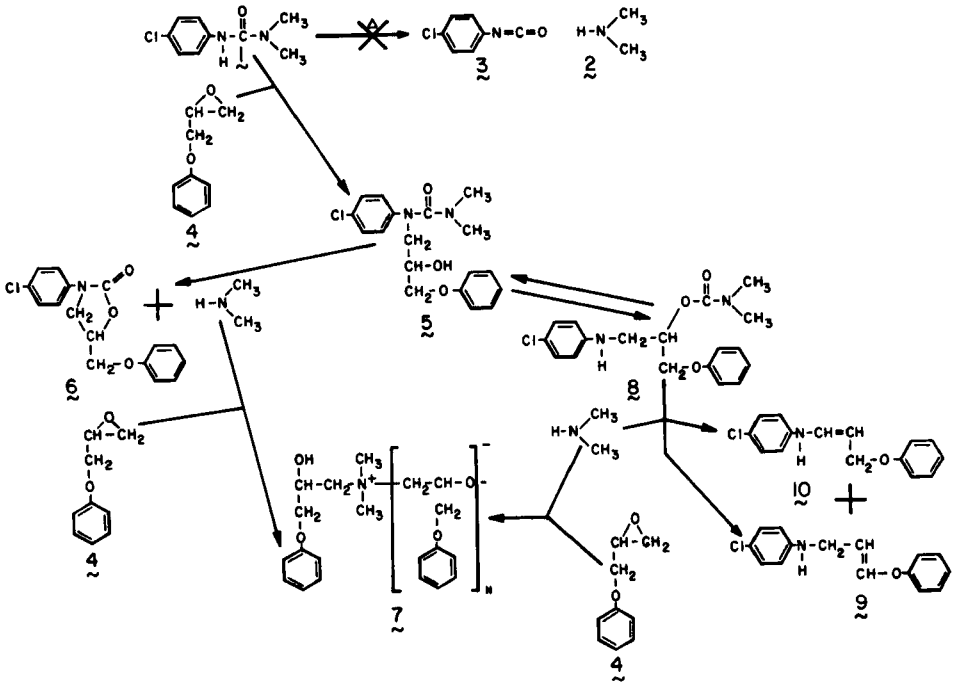


FIGURE 2 Carbon-13 NMR spectrum of a 1:1 molar ratio of phenyl glycidyl ether and N,N-dimethyl-4-chlorophenyl urea showing both the gem-dimethyl carbons of the starting urea, and quaternary amine terminated polyether, in addition to aromatic (▲) and carbonyl (*) carbons of the oxazolidone, and vinyl carbon (■) from the elimination product.

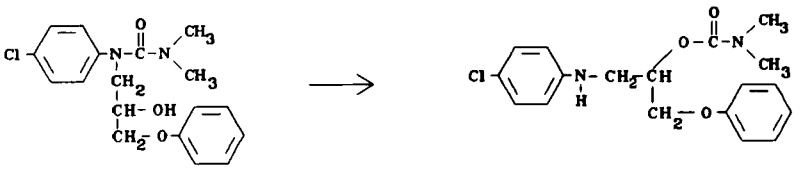


Scheme I

at 180°C is less than the ox:quat ratio of 1:1 that is predicted from the mechanism proposed in Equation 3 and Scheme 1. This observation suggests either that the oxazolidone formed along Path A reacts, *in situ*, during the reaction or that some other pathway (*i.e.*, Path B, Equation 4) may be significant. With either pathway, quaternary amine terminated poly(phenyl glycidyl ether), *7*, is formed.

The NMR spectra of the reaction products of *1* with phenyl glycidyl ether, *4*, at two molar stoichiometries are shown in Figures 3a and 3b. The spectra show the formation of oxazolidone functional groups, poly(phenyl glycidyl ether), quaternary amine functionality (as identified in Figure 2) and generally decreasing spectral complexity with increasing levels of phenyl glycidyl ether. These observations are consistent with the polymerization of the phenyl glycidyl ether with the dimethyl amine, which is formed in the reaction. This conclusion is also consistent with the reference spectrum of poly(phenyl glycidyl ether), Figure 3c, where the trend toward decreasing spectral complexity is at its furthest point.

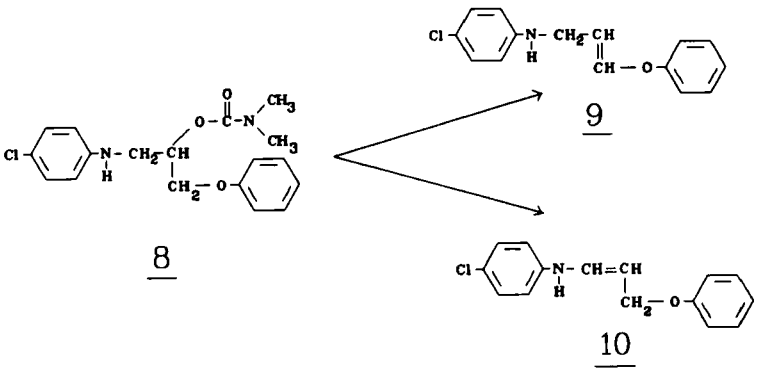
Along the other pathway, path B, rearrangement of *5* would be expected to afford the amino-dimethyl carbamate, *8*, (Equation 4).



5 8

Equation 4

Reaction along Path B would be expected to result in the formation of *8*, (Equation 4). The NMR data, showing the absence of the gem-dimethyl group suggests that, as is the case for *5*, this material is not stable enough to be observed. If formed, decomposition of this intermediate would likely occur through a decarboxylative deamination that results in the formation of dimethyl amine (without the concurrent formation of oxazolidone) and carbon dioxide, along with a range of the minor products (oligomeric phenyl glycidyl ether materials as well as unsaturated products derived from the suggested decarboxylative deamination reaction), Equation 5.



8 9 10

Equation 5

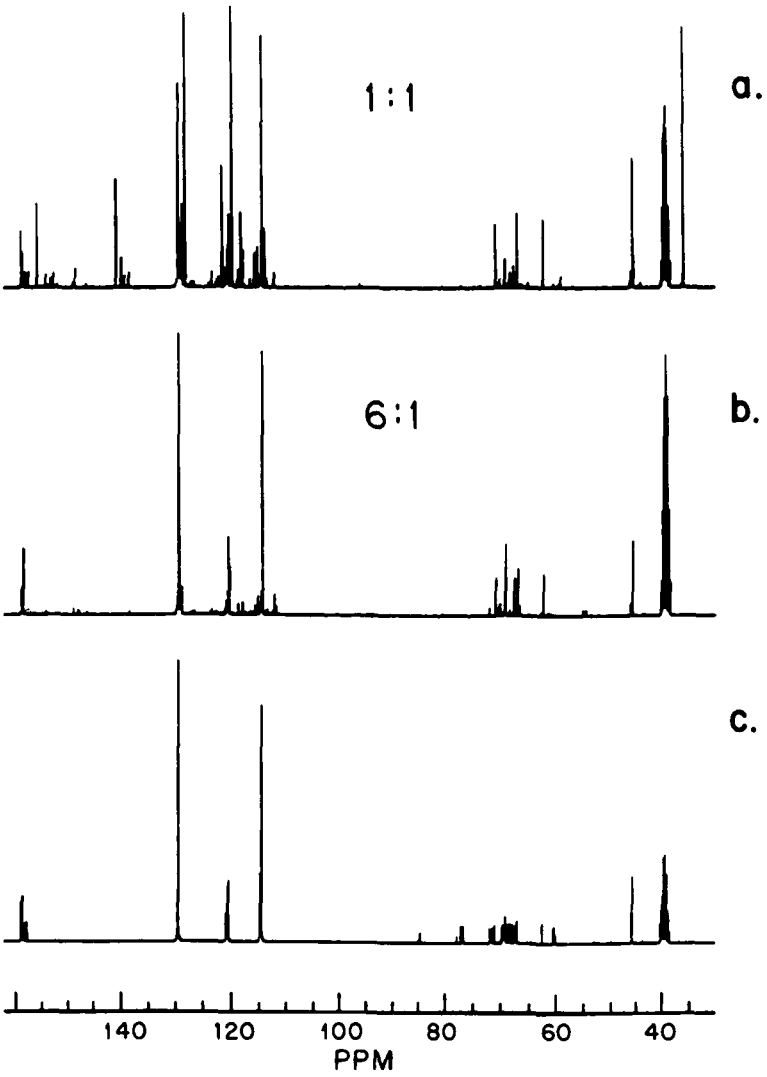


FIGURE 3 Carbon-13 NMR spectra comparing N,N-dimethyl-4-chlorophenyl urea:phenyl glycidyl ether reaction products at 1:1 (Figure 3a) and 6:1 (Figure 3b) molar ratios with a poly(phenyl glycidyl ether) obtained by the dimethyl amine polymerization of phenyl glycidyl ether, (Figure 3c).

The chemical shifts observed at 112 ppm (Figure 2) would be within the range of those for the unsaturated materials that would result from the decarboxylative deamination of *8*. This process would be entropically favored at elevated temperatures. This is consistent with reactions of *1* with *4* performed at 120°C and 180°C with 1:1 stoichiometry that show that higher ox/quat ratios are obtained at lower temperatures. At 120°C, an ox/quat ratio of nearly 1:1 is observed whereas at 180°C this ratio is about 0.1 The results suggest that the crosslinked network of epoxy adhesives formulated with *1* would have an increased amount of dangling ends as the amount of this accelerator in the adhesive formulations is increased, or as the

adhesive is cured at higher temperatures. These variations in adhesive formulation and cure process may result in variations in the mechanical properties of the final cured adhesive.

Stability of Oxazolidone Under Reaction Conditions

Control experiments have shown that the oxazolidone is thermally stable under the reaction conditions; no evidence of thermal disassociation into epoxy and isocyanate was observed after heating the material at 180°C. Heating the oxazolidone in the presence of hydroxy and amine epoxy materials (*i.e.*, 1,5 pentanediol and triethanol amine) at 180°C did not result in transesterification, nor did heating the oxazolidone with either dimethyl amine or isophorone diamine result in transamination. These control experiments suggest that the oxazolidone formed during the reaction is stable toward the hydroxy and amine functional materials characteristic of epoxy/amine condensation reaction.

Incorporation of oxazolidone in an epoxy/amine reaction mixture resulted in a noticable loss in carbonyl absorption at about 1700 cm^{-1}, Figure 4, in addition to the expected absorptions for the epoxy amine condensation reaction. The results suggest that the lower than expected ox/quat ratio observed in the NMR experiment may be the result of a reaction between the oxazolidone and an epoxy/amine polymerization intermediate involved in the cure reaction. This reaction, however, likely does not involve intermediates such as *5* or *8*, since their involvement would incorporate an ester moeity within the growing polymer chain resulting in an increase in carbonyl content rather than the reduction of carbonyl absorption that was observed in the IR experiment. The results suggest that the quat intermediate, *7*, may take part in the elimination reactions involving *8*, promoting reaction along path B. This would cause the formation of increased amounts of dimethyl amine with the concurrent formation of additional quat and a reduction of the ox/quat ratio.

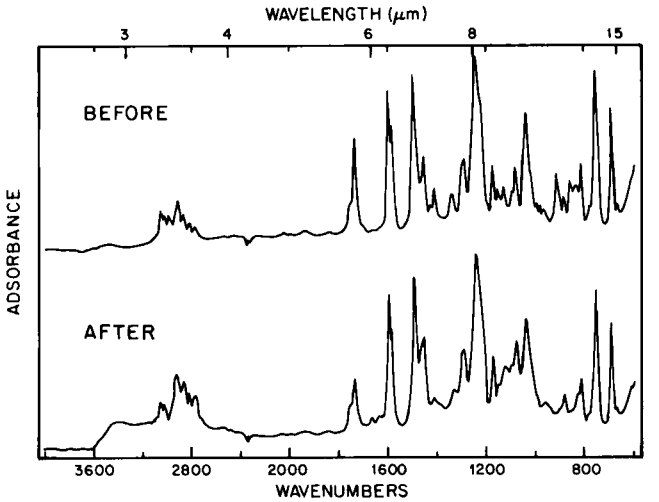


FIGURE 4 Infrared spectra demonstrating the stability of oxazolidone under amine-epoxy reaction conditions showing the reduction of carbonyl absorption at about 1700 cm^{-1}.

CONCLUSIONS

The reactions of N,N-dimethyl-4-chlorophenyl urea, *1*, with phenyl glycidyl ether have been examined in model epoxy adhesive formulations using Carbon-13 NMR. The results suggest that *1* can react with epoxy resins which are typical of those present in one-part adhesive formulations, and initiate polymerization and crosslinking reactions. In addition, the condensation reactions of *1* will generate dimethyl amine, a catalyst for the dicyandiamide crosslinking reaction for one-part epoxy adhesives.

The reaction of *1* with phenyl glycidyl ether generates oxazolidones and unsaturated materials in addition to dimethyl amine, and quaternary amine terminated polyethers. The latter two materials would be formed from equivalent amounts of epoxide functional groups but would not result in polymerization or crosslinking of the epoxy resin. This process would generate dangling ends in the crosslinked network if a crosslinkable epoxy were used.

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