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Mechanism of the Dicyandiamide/Epoxide Reaction

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ABSTRACT: A mechanism is proposed for the dicyandiamide (dicy) cure of epoxy resins based on the analysis of products formed by the reaction of a monofunctional epoxide with dicy and with cyanamide. Products were isolated from the uncatalyzed reaction mixtures using preparatory liquid chromatography and were characterized by FTIR, NMR, mass spectrometry, and elemental analysis. Both linear dicy/epoxide adducts and cyclical species were identified and the mechanism of the cyclization reaction was delineated. A mechanism for carbonyl generation during the later stages of cure was also found.

Introduction

The complex mechanism of the dicyandiamide (dicy) cure of epoxy resins has long intrigued chemical researchers. In addition to the usual changes associated with amine/epoxide reaction, early investigators, using infrared spectroscopy (IR), observed the apparent consumption of cyano (2180 and 2210 cm^{-1}) and hydroxyl (3400 cm^{-1}) groups, accompanied by the formation of new absorbance bands at 1740, 1690, and 1640 cm^{-1}.[1,2] On the basis, in part, of proton (^1H) nuclear magnetic resonance (NMR) studies of a model dicy/epoxide reaction,[3] the 1640-cm^{-1} band was assigned to an imino ester formed by the intermolecular addition of hydroxyl to the dicy cyano functionality. Absorbance bands at 1740 and 1690 cm^{-1} were assigned to carbonyls formed by the structural rearrangement of the imino esters into guanyl ureas. While this mechanism was consistent with the essential spectral features, ambiguities persisted, including disparities in the rate of disappearance of the two cyano bands and in the relative rates of new band formation. Furthermore, IR investigations were hampered due to dicy insolubility and the inherent inhomogeneity of the dicy/epoxy cure.[2,4,5]

In order to facilitate product analysis, Zahir[6] studied the base-catalyzed reaction of a monoepoxide, phenyl glycidyl ether (PGE), with both dicy and its monomer cyanamide. Product fractions were isolated by using size-exclusion chromatography (SEC) and were characterized by Fourier transform infrared spectroscopy (FTIR), carbon-13 (^{13}C) NMR, and mass spectrometry (MS). The dicy/PGE and cyanamide/PGE reactions were found to yield identical products, which were identified by Zahir as 2-iminooxazolidines and alkyl cyanamides. A mechanism was proposed in which the initially formed dicy/epoxide adducts cyclize via an intramolecular addition of hydroxyl to the cyano group, as shown in eq 1. These cyclized intermediates would then rapidly dissociate to form 2-iminooxazolidines and cyanamides (eq 2). Carbonyl formation was attributed to the slow subsequent rearrangement of the 2-iminooxazolidines into cyclic ureas (eq 3). In a curing system, Zahir felt that cyclization would be relatively rapid, and that cross-linking would then occur via the addition of epoxide to the generated imine and urea functionalities, as well as through etherification.

More recently, FTIR studies of both catalyzed[7] and uncatalyzed[8] dicy/epoxy cures have been interpreted in terms of the Zahir mechanism. However, while Zahir believed that cyclization occurred at a rapid rate relative to amine/epoxy addition, these later studies revealed the apparent persistence of substantial amounts of alkylated dicy in the cured systems. Further, the distribution of reaction products appeared to be dependent on cure temperature, with higher temperatures promoting cyclization and structural rearrangement and lower temperatures favoring alkyl dicy accumulation. On the basis of differential scanning calorimetry (DSC) studies of tertiary amine catalyzed systems, it has been reported that the initially formed dicy/epoxy adducts are stabilized against cyclization via the consumption of hydroxyl groups by etherification reactions.[9] Etherified alkyl dicys have also been identified as the predominant products isolated from a base-catalyzed dicy/PGE reaction.[10]

The present study began as an attempt to determine the kinetic parameters for the several reactions comprising the Zahir mechanism, using a dicy/monoepoxide reaction as a model. Mixtures were isothermally reacted in a DSC over a range of temperatures and times and were then analyzed by high-performance liquid chromatography (HPLC). By quantification of product formation, it was hoped that the relative rates of individual reactions could be discerned. Chromatographic peaks are tentatively assigned to Zahir structures based on their apparent relative rates and order of formation. However, discrepancies were encountered, which necessitated the isolation and identification of individual products and led to a reevaluation of the Zahir mechanism.

Experimental Section

For the initial kinetic study, samples were made by reacting dicy/monoepoxide mixtures (10–20 mg) in a Perkin-Elmer DSC-2 prior to analysis by HPLC. In order to make specific product identifications, individual products were isolated by using reversed-phase preparatory liquid chromatography (PLC), from dicy/monoepoxide mixtures (ca. 0.5 g), which had been reacted in a preheated oven. Product separation was monitored by HPLC, using conditions developed for the initial kinetic study, and isolated products were assigned to the several chromatographic peaks of the initial HPLC kinetic study based on HPLC retention times.

Reactions were run without a catalyst, in order to limit etherification and simplify the resultant product mixtures. Due to the high temperatures required for the uncatalyzed dicy/epoxide reaction (>150 °C), it was necessary to use a high molecular weight, low volatility monofunctional epoxide. The methyl gly-

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cidyl ether of Bisphenol A (MGEBA) was synthesized for this purpose. Bisphenol A (Aldrich, gold label, 99+% pure) was partially methylated by using dimethylsulfate in methanol. Following this reaction, the mixture of products was dissolved in aqueous NaOH. Dimethyl Bisphenol A was first extracted from the basic solution by washing with cyclohexane, and then the monomethyl Bisphenol A was extracted by using methylene chloride. MGEBA was formed by reaction of the monomethyl Bisphenol A with excess epichlorohydrin in NaH/THF. Dicyandiamide and cyanamide, 97% and 99+% pure, respectively, were purchased from Aldrich and were used without further purification.

Preparatory Liquid Chromatography. Samples of unmilled dicy and MGEBA were hand mixed and placed in a preheated oven. No attempt was made to exclude air from the reacting mixtures. Solutions for PLC separation were made by dissolving the product mixtures in 100% THF, a solvent in which the excess dicy was nearly insoluble. These solutions were filtered to remove the excess dicy, and then distilled water was added in order to adjust the polarity of the solvent to that of the PLC mobile phase.

The PLC apparatus consisted of a 50 cm × 1.5 cm i.d. glass column, hand-packed with a Waters Preparative C-18 bonded phase, silica gel packing material, with a particle size ranging from 55 to 105 μm in diameter. The mobile phase consisted of THF, acetonitrile, or methanol adjusted to the desired polarity by the addition of distilled water. HPLC UV-grade solvents were used for this purpose. The mobile-phase compositions are designated in the text by the volume percentage of organic solvent contained in the mixture. A single low-pressure Waters solvent pump was used, and solvent flow rates ranged between 3 and 15 mL/min. Products were detected by a Waters Model 500 refractive index (RI) detector, equipped with a strip chart recorder, and the mobile phases were by necessity isochratic. Fractions were collected by following the RI trace and were subsequently analyzed by HPLC.

A Waters HPLC system equipped with a Model 660 solvent programmer, two M-6000A pumps, a Model 441 UV detector and a Model 730 data module, and a reversed-phase, μBondapak C18 column (30 cm × 3.9 mm i.d.) packed with 10-μm packing material was used for this purpose. Solvent mixtures of THF: H_2O = 50:50 to 90:10 were run at a flow rate of 1.0 mL/min, using a variety of programmed gradients and run times. Detector wavelengths of 280 and 229 nm were independently used. Each injection contained 15 μL of sample solution. Following HPLC analysis, solvents were removed by using a rotary evaporator. The isolated products were then dried overnight in a room-temperature vacuum oven prior to further analysis.

Product Analyses. SEC analyses of the products were performed by using three IBM, two A and one C, low molecular weight, 5-μm columns in series. A Waters Model 840 system controller was used for solvent programming and data acquisition. The system was equipped with a Waters Model 401 RI detector and an Model 6000A solvent pump. The mobile phase consisted of 100% THF at a flow rate of 1 mL/min. The column temperature was 40 °C.

FTIR spectra were obtained by using a Perkin-Elmer 1550 FTIR spectrometer, equipped with a 7500 series data station. Sixty-four scans at a resolution of 4 cm^{-1} were made of films cast on NaCl plates from methylene chloride solutions of the isolated products. ^1H and ^{13}C NMR spectra were obtained by using a Bruker MSL-200 FTNMR spectrometer at 200.13 and 50 MHz, respectively. Approximately 1% solutions of the products in $CDCl_3$ were used with TMS as an internal standard. Samples in 5-mm-o.d. tubes were scanned 20 times for proton NMR spectra, and samples in 10-mm-o.d. tubes were scanned 200 times for ^{13}C NMR spectra. Fast atom bombardment mass spectra (FABMS) were obtained by using a VG70-250SE mass spectrometer, on samples imbedded in a nitrobenzyl alcohol matrix.

The further reactions of isolated products with MGEBA were studied. Mixtures were prepared for DSC analysis by combining the isolated products with MGEBA directly in DSC aluminum sample pans. Compositions were determined by weighing the sample pans on a microbalance before and after the addition of each of the reactants. Mixtures were reacted in the DSC both isothermally and by temperature scanning, and the resulting product mixtures were analyzed by HPLC.

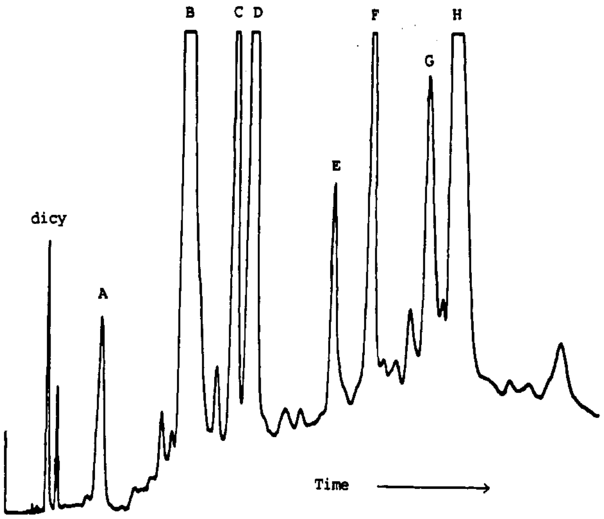


Figure 1. HPLC chromatogram of dicy/MGEBA reacted at 187 °C for 60 min; THF/H_2O = 50–90%, over 40 min, at grad 6, analyzed at 229 nm.

Results and Discussion

A typical HPLC chromatogram of an uncatalyzed dicy/MGEBA reaction mixture is shown in Figure 1. In addition to the peaks assigned to dicy and MGEBA (peak B), several prominent product peaks are evident. Structures were tentatively assigned to these peaks based on apparent order of formation, comparison with the cyanamide/MGEBA product mixtures discussed below, and HPLC column elution times. In general, longer elution times are expected for less polar, more highly substituted species. Thus, peak A was assigned to monosubstituted species and peaks C and D to disubstituted species, while a complex assortment of higher molecular weight products were thought to comprise peaks E–H. During the course of the reaction, the relative areas of peaks C and D were observed to slowly increase. Following completion of epoxide consumption, further heating appeared to result in the transformation of C into D. Consequently, peak C was assigned to the disubstituted 2-iminooxazolidine, while peak D was assigned to a cyclic urea, in accordance with the Zahir mechanism.

Peaks C and D each appeared to contain a single, well-resolved component, which could be readily isolated by using PLC. Isolation was achieved by using repetitive separations with 55% THF as the mobile phase. FTIR spectra of isolated peaks C and D are shown in Figures 2 and 3, respectively. While minor features indicative of cross-contamination are evident, several of the major absorbance bands appear to be unique to each of the isolated materials. In Figure 2, the large absorbance band at 1650 cm^{-1}, assigned by Zahir to the 2-iminooxazolidine, would appear to confirm the tentative designation of peak C. However, the appearance of a cyano absorbance band at 2205 cm^{-1} contradicts this assignment. While the presence of these two bands might be indicative of a substituted dicy, the possibility also existed that peak C contained two compounds of similar polarity, which were indistinguishable by HPLC. The spectrum of peak D, on the other hand, revealed only a single structurally significant absorbance band, located at 1740 cm^{-1} in the carbonyl region. Previously reported in studies of the dicy/epoxy cure,[1,2,7,8] this band apparently confirmed the identity of peak D as the cyclic urea rearrangement product described

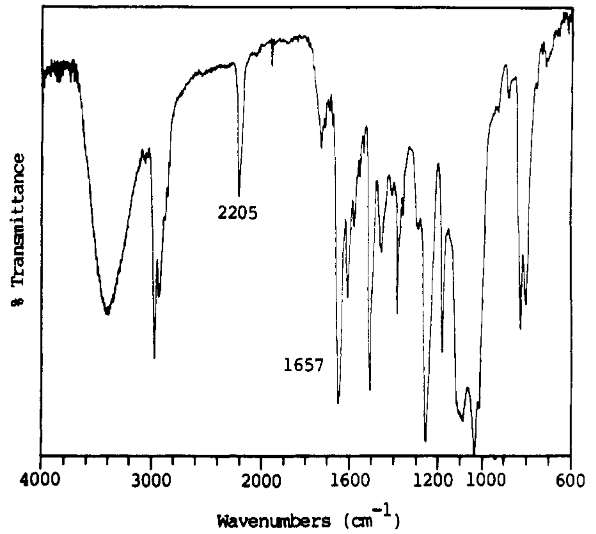


Figure 2. FTIR spectrum of isolated peak C.

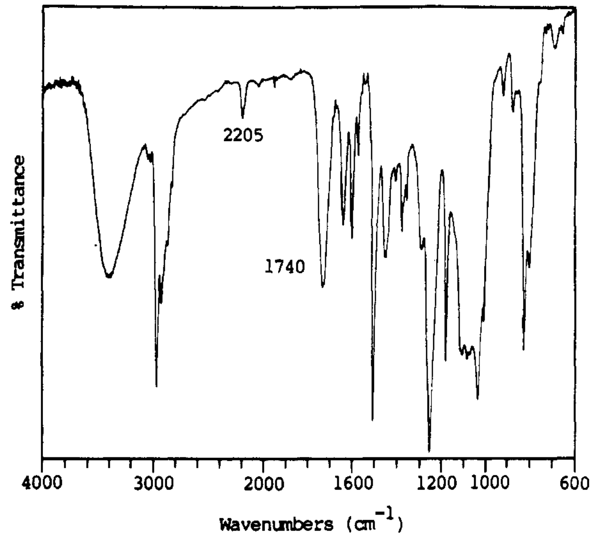
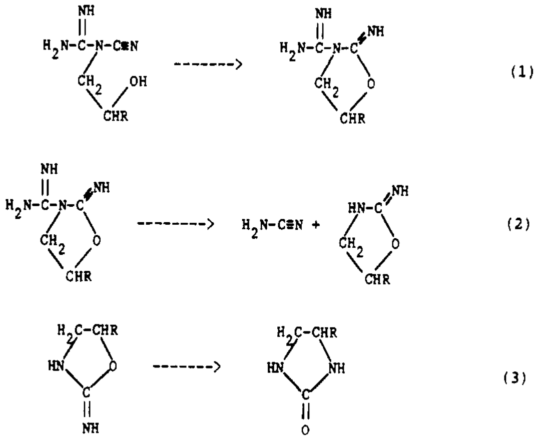


Figure 3. FTIR spectrum of isolated peak D.

Scheme I



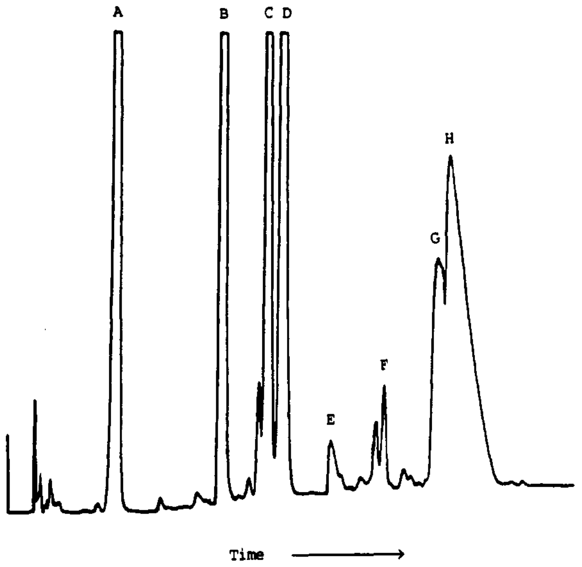


Figure 4. HPLC chromatogram of cyan/MGEBA product mixture; THF/H_2O = 50–90%, over 40 min, at grad 6, analyzed at 280 nm.

by Zahir. Peak A was also isolated, by using 70% acetonitrile in water. FTIR characterization revealed a spectrum that was nearly identical with that of peak D. No evidence of imide or cyano structures was found, and the peak appeared to be comprised almost entirely of a monosubstituted cyclic urea.

Due to the complexity of the product mixture comprising the less polar region in the chromatogram of Figure 1, individual products could not be readily isolated. These products were thought to consist of both multiply substituted dicys and the more highly substituted analogues of C and D. Using HPLC analysis to follow the dicy/MGEBA reaction, an attempt was made to discern the relationship of C and D to these less polar products. Observations revealed the simultaneous growth of both C and D and the less polar peaks during the course of the dicy/MGEBA reaction. Continued heating beyond completion of epoxide consumption did not appreciably change the size of the less polar peaks, apparently indicating a lack of multisubstituted dicys in these peaks. However, the exact relationship of C and D to the several low polarity peaks remained unclear.

Products Isolated from Cyanamide/MGEBA. In order to clarify the ambiguities posed by the FTIR analysis of peak C and to obtain the quantity of material necessary to study the further reactions of C and D with MGEBA, an attempt was made to obtain these intermediates from the reaction of cyanamide with MGEBA. This reaction was expected to yield 2-iminooxazolidines, identical with those formed in the dicy/MGEBA reaction (see Scheme I), via cyclization of the initially formed alkyl cyanamides. However, advantage could be taken of the increased solubility and high reactivity of cyanamide relative to dicy, in an effort to obtain mixtures greatly enriched in the desired low molecular weight, initial products. Difficulties were encountered due to the competitive dimerization of cyanamide into dicy, which is unreactive at the temperature used. In addition, the use of a large excess of cyanamide results in a highly exothermic reaction, accompanied by charring and resin degradation. These problems were overcome by continually adding fresh cyanamide to the reaction mixture at set intervals over the course of the reaction. In this way, a high effective concentration of cyanamide was maintained, which allowed high concentrations of initial products to be formed while avoiding an explosively exothermic reaction.

An HPLC chromatogram of a cyanamide/MGEBA mixture reacted at 100 °C is shown in Figure 4. While the chromatographic peak placement is identical with that of the dicy/MGEBA mixture, the concentration of the less substituted polar products is higher. Especially evident is the high concentration of peak A, tentatively assigned to the 1:1 adduct of cyanamide and MGEBA. Products

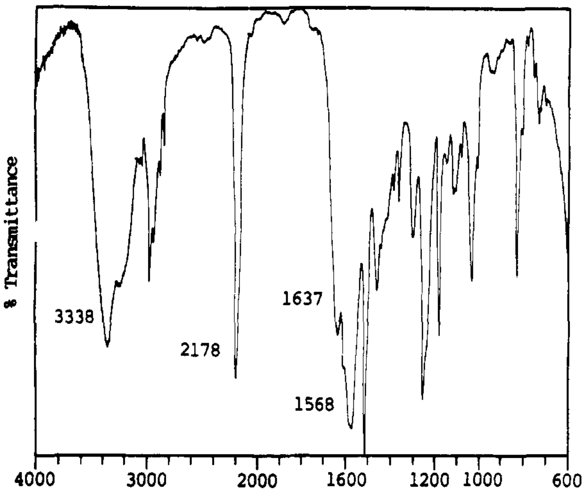


Figure 5. FTIR spectrum of product I.

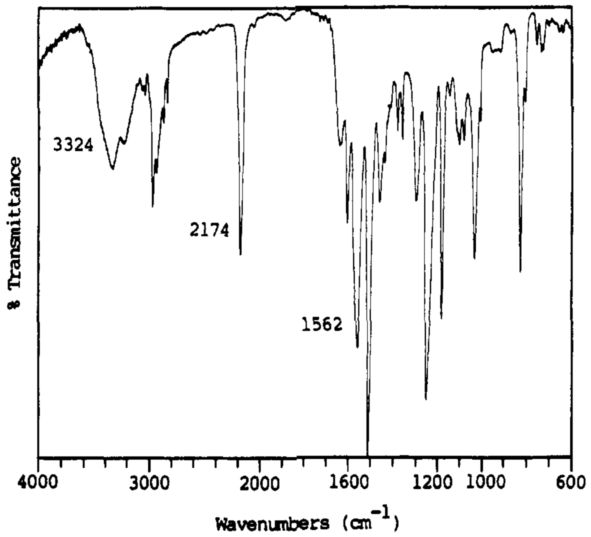


Figure 6. FTIR spectrum of product II.

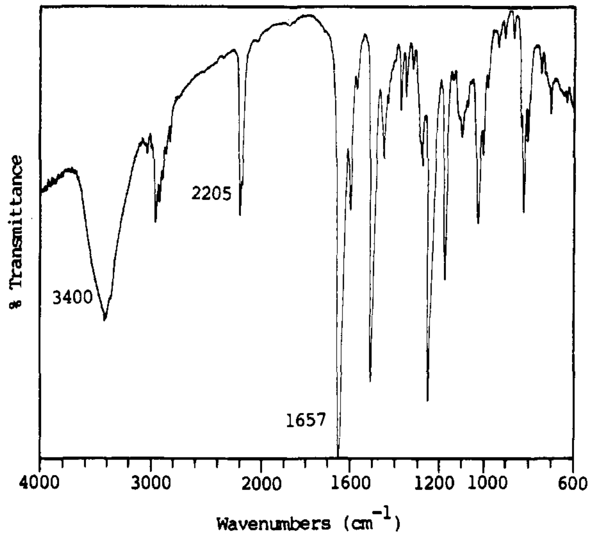


Figure 7. FTIR spectrum of product III.

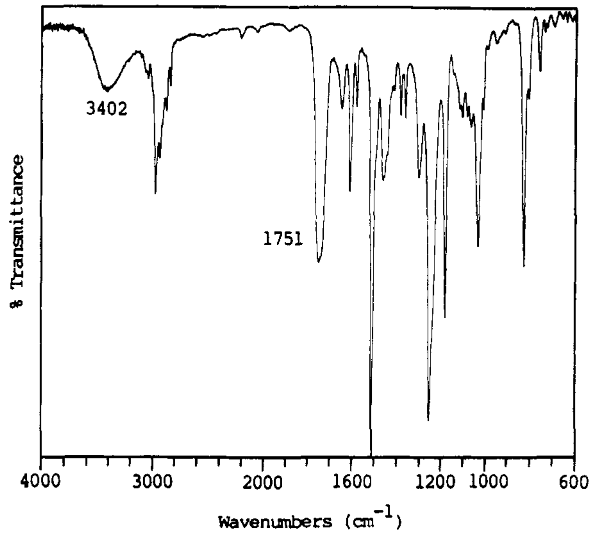


Figure 8. FTIR spectrum of product IV.

were isolated in a manner similar to that used for the dicy/MGEBA reaction mixture and are here designated by Roman numerals to indicate their apparent order of formation. Products I and III were isolated from peaks A and C, respectively, while products II and IV were both isolated from peak D. Product I was isolated by using 60% acetonitrile/water. Isolation of products II–IV was accomplished by repetitive separations, by using two mobile-phase combinations. Product II was first isolated from products III and IV by using 70% acetonitrile/water. Products III and IV were then separated from one another by using 55% THF/water.

An FTIR spectrum of isolated product I, shown in Figure 5, reveals a large cyano absorbance band at 2178 cm^{-1}, supporting the tentative designation of this compound as the 1:1 adduct of MGEBA and cyanamide. Attempts to determine the molecular weight of product I using gas chromatography (GC)/MS were only partially successful. While a small portion of the isolated material was volatilized and eluted by the GC, the bulk of the sample appeared to undergo reaction, yielding higher molecular weight compounds which could not be volatilized without degradation. For the GC elutable material, a molecular weight of 342 amu was determined, apparently confirming its identification as the monoalkyl cyanamide.

The spectrum of product II, shown in Figure 6, also reveals a cyano absorbance band at 2174 cm^{-1}. While this spectrum is similar in appearance to that of product I, the ratio of the height of the cyano band to the height of the phenyl stretch at 1511 cm^{-1} in this spectrum is about half of that observed in the spectrum of product I. Thus, product II appeared to be the 2:1 adduct of MGEBA and cyanamide. The spectra of products III and IV, shown in Figures 7 and 8, respectively, are identical with those of peaks C and D isolated from the dicy/MGEBA reaction mixture, supporting the contention that identical products are formed in the two reactions. The carbonyl in the spectrum of product IV has been shifted to 1751 cm^{-1}, compared to the spectrum of peak D in Figure 3, possibly due to the increased purity and lower moisture content of this material when analyzed. The spectrum of product III again exhibits both the imino and cyano absorbance bands, making unambiguous identification impossible.

Attempts to analyze products II–IV by GC/MS were unsuccessful, again due to the difficulty in volatilizing or ionizing these materials. In order to gain some insight into the relative molecular sizes of the several isolated species, analyses were conducted by using SEC. Products II–IV were found to be of comparable size, with II slightly larger than III, and III slightly larger than IV. Product I, on the other hand, appeared to be intermediate in size between these compounds and MGEBA. This was in agreement with the initial assumption that product I was

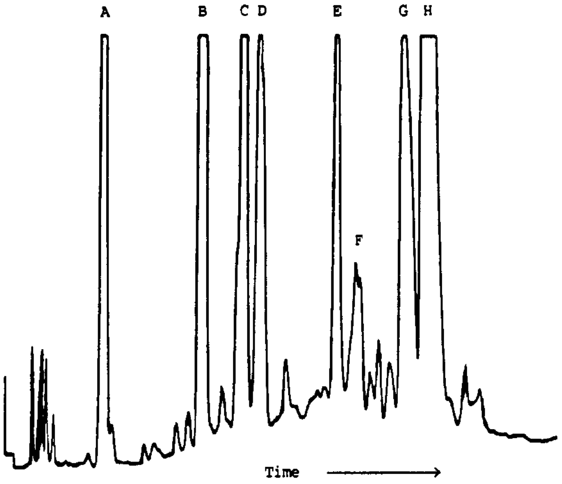


Figure 9. HPLC chromatogram of (1:4.5) I/MGEBA reacted at 167 °C for 15 min; THF/H_2O = 50–90%, over 40 min, at grad 6, analyzed at 229 nm.

a monoalkylated species, while II–IV were dialkylated. HPLC observations revealed that heating a neat sample of product II to 167 °C for several minutes, resulted in its conversion into product III and then into product IV. Since the SEC results indicated that product III was of virtually the same molecular size as product II, it appeared that this thermal transformation occurred as the result of an intramolecular reaction, presumably hydroxyl addition as described by Zahir (Scheme I).

Further Reaction of Isolated Products with MGEBA. The further reactions of the isolated species with MGEBA were studied by reacting mixtures in the DSC and analyzing the resulting product mixtures by HPLC. It was hoped that this study not only would provide information on the kinetics of the later stage reactions but also would allow the identification of the several less polar peaks in Figure 1. A chromatogram of the mixture obtained from the reaction of product I with MGEBA is shown in Figure 9. In this example a 1:4 mixture of product I and MGEBA was isothermally reacted at 167 °C for 15 min. The resulting chromatogram is in appearance identical with those obtained from the dicy/MGEBA and cyanamide/MGEBA reaction mixtures. Thus, product I appeared to be the initial product from which all other products could be formed. The reaction of product II with MGEBA produced a similar product mixture, containing all other products except product I, further supporting the hypotheses that product II is the 2:1 analogue of product I.

Attempts were also made to react products III and IV with MGEBA by using similar conditions. However, HPLC analyses of the product mixtures revealed that no reaction of products III or IV had occurred. While some of the MGEBA was consumed by these reactions and product III was observed to slowly transform into product IV, the sum total of III and IV in the reaction mixtures did not change. Further, no products identifiable as peaks F, G, or H appeared in the chromatograms. Attempts to promote the reaction by catalyzing with BDMA or product I failed, as did the use of extended reaction times or temperatures up to 220 °C. Peaks C and D, isolated from the dicy/MGEBA product mixture, were found to be similarly unreactive toward further epoxide addition, as were the products obtained by the thermal conversion of product II.

The nonreactive nature of products III and IV was surprising. According to the Zahir mechanism, as disubstituted cyclic products, these compounds should have been reactive toward epoxide addition through either the imine or amide functionality. Further, on the basis of the tentative identification of product II as a dialkyl cyanamide, it was difficult to understand the high reactivity of this compound toward epoxide addition, in the absence of cyclization. Also unclear was the nature of the thermal transformation, which rendered product II inactive.

In an effort to aid the spectral characterization of product III and to help in understanding its unreactive nature, the compound 2-imino-3-phenyloxazolidine was synthesized as a model, following the work of Catsiff et al.[11] FTIR analysis of the model oxazolidine revealed a strong imino absorbance band at 1670 cm^{-1}, comparable to that observed in the spectrum of product III. However, the spectrum of the model did not exhibit a cyano absorbance band, which would have been present if ring formation were an equilibrium reaction. Mixtures of the 2-imino-3-phenyloxazolidine with MGEBA were also found to be quite reactive toward imine/epoxide addition, as evidenced by HPLC analysis. Proton FTNMR characterization of the model oxazolidine revealed a peak at 5.48 ppm assigned to the imino proton. This proton was exchangeable with deuterium from added D_2O, resulting in complete elimination of the NMR peak. The FTNMR spectrum of product III revealed a similar peak, at 5.10 ppm, which was not found in the FTNMR spectra of products I and II. Although this peak has a chemical shift similar to the imine group of the model compound, all attempts to exchange this proton with D_2O failed. A further discussion of the ^1H NMR analysis of isolated products I–III is presented later in this text.

FABMS and Elemental Analysis of Products I–III. To facilitate further characterization, attempts were made to obtain highly purified materials. This was done by repetitive isolations with the PLC and, in the case of products I and III, by recrystallization from 100% methanol and 2% water in methanol, respectively. Eventually, enough material was purified by this procedure to allow characterization by ^{13}C FTNMR. Further, the ultrapure nature of these materials made it possible to obtain elemental and, most importantly, MS analyses. As discussed, initial attempts to determine molecular weights by the techniques of GC and solid probe MS had failed due to the reaction or degradation of the isolated materials either at the temperatures required for volatilization or in the electron beam. However, using the relatively mild technique of FABMS, it was possible to obtain and analyze stable parent ions.

FABMS spectra of products I–III are shown in Figure 10, and the mass of the protonated parent ions are labeled. Molecular weights determined by this technique are listed in Table I, along with the results of elemental analysis. Products I and II were found to have molecular weights of 382 and 680 amu, respectively. This indicated that products I and II were in fact the 1:1 and 2:1 adducts of MGEBA and dicy, respectively, and not alkyl cyanamides as originally believed. These designations are confirmed by elemental analysis, as shown in Table I. Product III was found to have a molecular weight of 663, indicating that a weight loss of 17 amu occurs during the transformation of product II into product III. Elemental analysis confirms that this weight loss is due to the elimination of ammonia.

The structure of product III and mechanism of its formation are illustrated in Scheme II. In contrast with the mechanism proposed by Zahir, cyclization of the alkyl dicy does not appear to occur through hydroxyl/cyano addition. Rather, cyclical compounds are formed via the

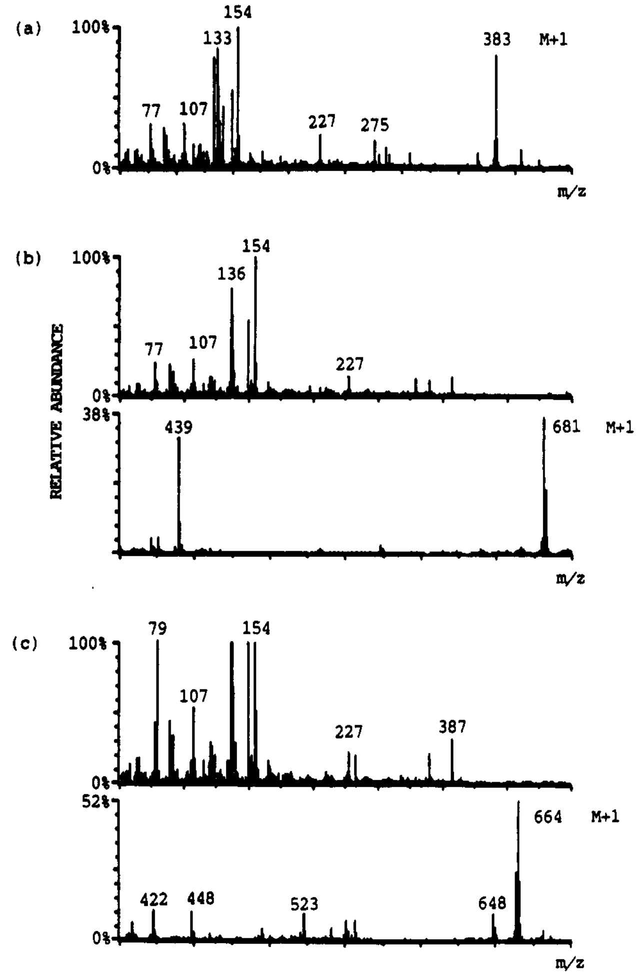


Figure 10. FABMS spectra of (a) product I, (b) product II, and (c) product III.

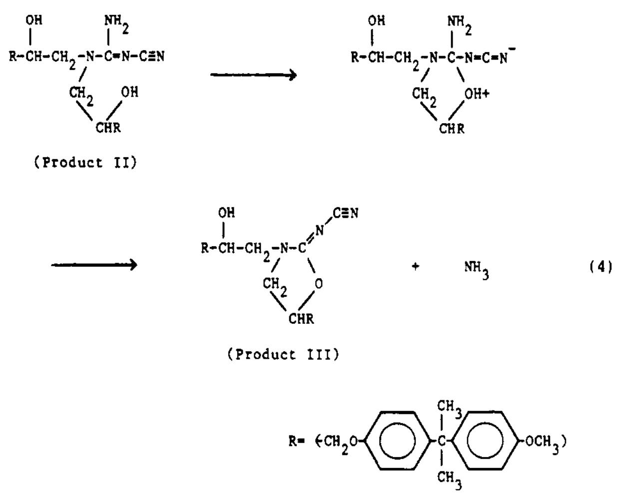
Table I
MS and Elemental Analysis of Isolated Products

product		mass, amu	elem anal., %		
			C	H	N
I	exptl	382	64.14	6.41	14.22
	theor		65.97	6.81	14.66
II	exptl	680	69.77	7.25	8.20
	theor		70.59	7.06	8.24
III	exptl	663	71.99	6.52	6.24
	theor		72.40	6.79	6.33

intramolecular nucleophilic substitution of hydroxyl at the imide carbon, resulting in the elimination of a molecule of ammonia. The cyclized product, a 2-cyanimidooxazolidine, contains no labile protons and is, therefore, not reactive toward further epoxide addition. By acting concertedly, the cyano-substituted imide group behaves very much like a carbonyl group in this reaction. This mechanism is similar to that previously proposed for the reaction of epoxide with substituted ureas.[12,13] Although the cyano and imido groups remain intact during this reaction, cyclization results in the spectral shift of IR absorbance bands assigned to these functionalities, from 2180 to 2205 cm^{-1} for the cyano and from 1570 to 1650 cm^{-1} for the imido band. Similar shifts attributable to cyclization were also observed in the NMR spectra of these materials, as will be discussed. The further implications of ammonia generation on the structure of the cross-linked resin will also be addressed below.

The fortuitous formation of alkyl dicys in the cyanamide/MGEBA reaction mixtures apparently occurred through the further addition of excess cyanamide to the initially formed alkyl cyanamides. Cyanamide dimerizations of this kind appear to be responsible for the similarities of the dicy/epoxide and cyanamide/epoxide reaction mixtures. The original erroneous GC–MS molecular weight determination for product I appears to have resulted from the presence of monoalkyl cyanamide as a minor, yet easily volatilized, contaminant in the initially isolated material.

Scheme II



Purified products I–III were characterized by ^{13}C FT-NMR, in order to confirm the proposed structures. For purposes of reference, a ^{13}C NMR spectrum was also obtained for MGEBA and is shown in Figure 11a. Several peaks are labeled to designate their assignment in the accompanying structure. Particularly instructive in the characterization of the isolated reaction products are the chemical shifts of the carbons comprising the oxirane functionality of the MGEBA molecule. In Figure 11a, these carbons are assigned to peak C at 46.1 ppm and peak D at 51.5 ppm. For the sake of clarity, these carbons will be referred to as carbon 1 (C1) and carbon 2 (C2), respectively.

The formation of product I, via the reaction of MGEBA with dicy, shifts the peaks assigned to C1 and C2 to 46.22 and 71.01 ppm, respectively, as shown in Figure 11b. This is indicative of the chemical change of C1 and C2 from oxirane carbons to a secondary amine substituted carbon and a hydroxyl-substituted carbon, respectively. In ^{13}C NMR spectrum of disubstituted product II, shown in Figure 11c, the two C1 and two C2 carbons are each assigned to a single peak, at 55.44 and 70.74 ppm, respectively. While this spectrum is indicative of the symmetric nature of the substitution, the downfield shift in the peak assigned to C1 reveals the change in environment of C1, from that of secondary amine substituted carbon to that of a tertiary amine substituted carbon.

In contrast to the spectrum of product II, the spectrum of disubstituted product III, shown in Figure 11d, exhibits two peaks assigned to C1, at 49.7 and 51.8 ppm, which are indicative of the now different environments of these two amine-substituted carbons. Further, only one of the two C2 carbons retains the chemical shift assignable to a hydroxyl-substituted carbon. The other has been shifted downfield to 78.2 ppm and is visible partially occluded by the chloroform triplet. The shift of this C2 peak occurred as a result of the intramolecular reaction of the hydroxyl functionality adjacent to the C2 carbon.

A similar downfield shift occurs in the ^1H NMR spectrum of product III. As illustrated in Figure 12, the proton attached to the C2 carbon (=CHOH) is assigned

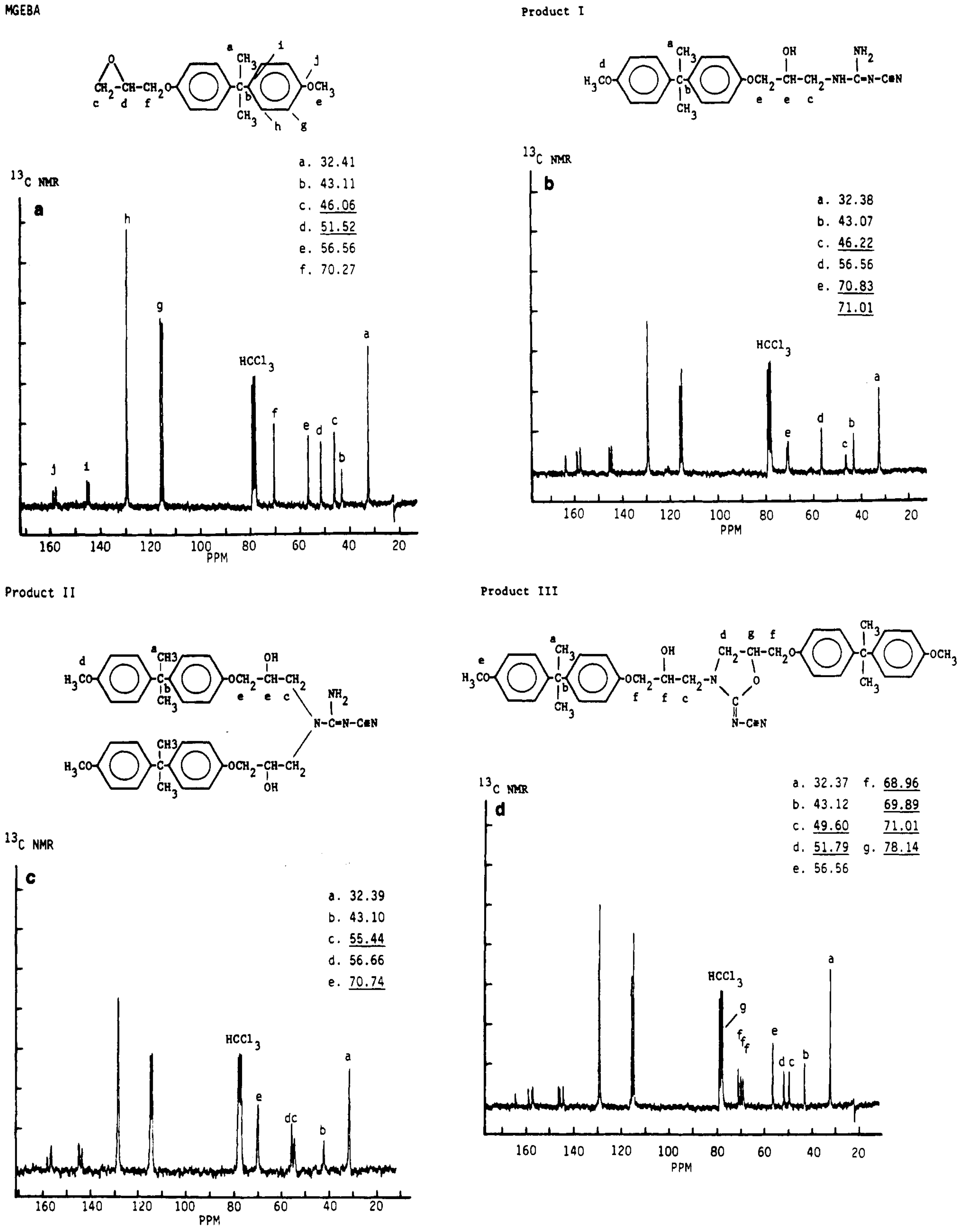


Figure 11. ^{13}C NMR spectra and structures of (a) MGEBA, (b) product I, (c) product II, and (d) product III.

to a peak at 4.3 ppm in the ^1H NMR spectra of products I and II. Peak area integration reveals one such proton for product I and two such protons for product II, in line with their respective structures. However, the spectrum of product III shows only one. The other proton has been shifted by cyclization to a peak at 5.1 ppm, where it was originally mistaken for an imine proton. It is believed that the appearance of this peak may also have misled earlier researchers in their characterization of unresolved product mixtures.[3] Due to difficulties with line broadening, the hydroxyl protons could not be readily quantified in these materials. However, the ^1H FTNMR spectrum of product I did reveal deuterium exchangeable peaks at 6.5 and 6.2 ppm, assigned to secondary and primary amine protons, respectively. The spectrum of product II was found to contain only the primary amine peak at 6.2 ppm,

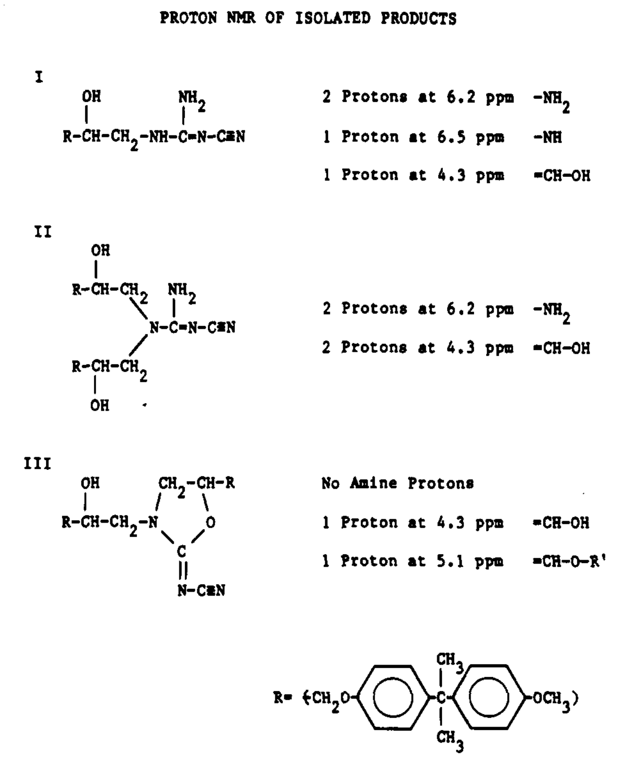


Figure 12. ^{1}H NMR spectra and structures of products I–III.

while the spectrum of product III exhibited no peaks in this region, supporting the proposed structures of these products.

The formation of product III by intramolecular substitution, as depicted in Scheme II, results in the liberation of ammonia. Similarly, the cyclization of more highly substituted dicys is expected to result in the liberation of alkyl amines. Once formed, at the temperatures required for dicy/epoxide reaction both the ammonia and alkyl amines can be expected to react rapidly with epoxide, ultimately forming tertiary amine adducts. Therefore, an attempt was made to find these products in the dicy/MGEBA reaction mixtures. Since these products were expected to be relatively nonpolar, the search began with chromatographic peaks G and H, shown in Figure 1. When repeated PLC separations were used, it was possible to isolate the major component of peak H in relatively pure form. Analysis by FABMS revealed a molecular weight of 911 amu, confirming the identity of this compound as the 3:1 adduct of MGEBA and ammonia.

An FTIR spectrum of this compound, designated as product V, is shown in Figure 13. Comparison of this spectrum with that of the starting MGEBA reveals little in the way of distinguishable differences, aside from the loss of epoxide and formation of hydroxyl. Thus, it would have been difficult to detect this compound in a dicy/epoxide product mixture by means of spectral subtraction, as was used by Davidson.[8] On the basis of FTIR analyses, product V appears to comprise the bulk of the material isolated from both peak G and peak H. It is believed that these peaks represent diastereomeric forms of product V.[14] As the 3:1 adduct of MGEBA and ammonia, product V has three chiral centers and thus eight stereoisomers. Due to molecular symmetry, these isomers are divided into two diastereomeric sets, one containing two isomers and the other six. These diastereomers are separable by HPLC, and this 1:3 diastereomer ratio is reflected in relative areas of peaks G and H over a wide range of product compositions.

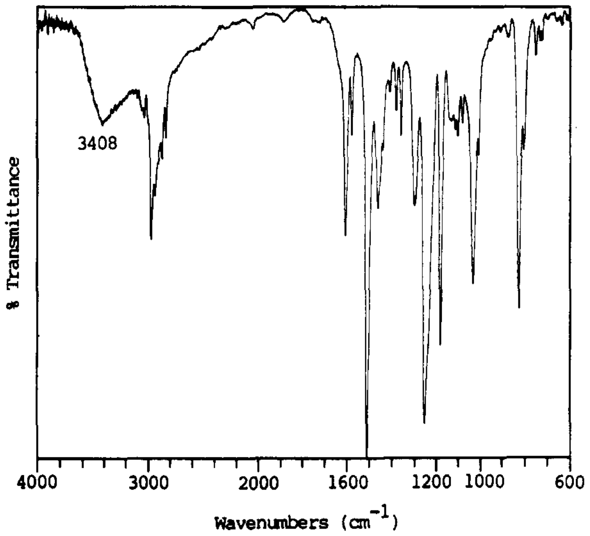
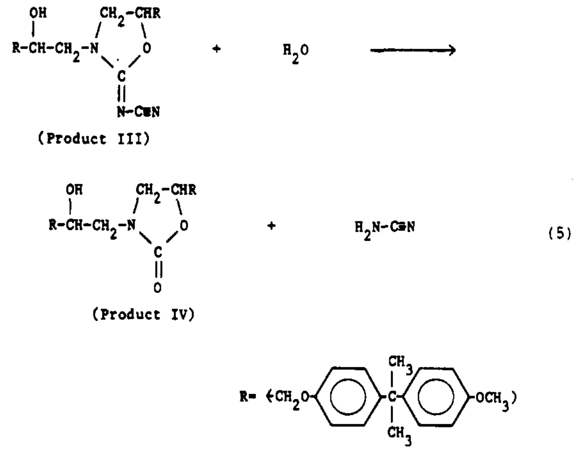


Figure 13. FTIR spectrum of product V.

Scheme III



Carbonyl Formation. When heated with MGEBA or when formed from product II, product III appears to slowly transform into product IV. FTIR analysis has revealed that this transformation results in the disappearance of both the imide and cyano functionalities of product III and the formation of a carbonyl group. Given the structure of product III, it is clear that this transformation cannot be explained in terms of a simple rearrangement reaction, as proposed by Zahir. In order to determine the reaction responsible, attempts were made to form product IV directly from product III. In pure form, product III was found to be a relatively stable compound. It could be heated for several hours at 167 °C without weight loss or structural change as determined by HPLC. However, heating product III in the presence of water under identical conditions resulted in the almost complete transformation of product III into product IV. The structure and mechanism of formation of product IV is depicted in Scheme III. Carbonyl formation in this case occurs via hydrolysis of the imide bond. FABMS analysis of isolated product IV revealed a molecular weight of 639 amu, confirming the identity of this compound as a disubstituted 2-oxazolidone. Thus, water appears to play an important role in determining the final structure of a dicy-cured epoxy.

The combined evidence supports the proposed structures of products I–V. Cyclization of alkylated dicys appears to occur via an intramolecular nucleophilic substitution reaction. This reaction liberates ammonia and/or alkyl amines, which rapidly react with epoxide to form tertiary amines. Carbonyl formation results, at least in part, from the hydrolysis of the imide bonds. Although based on the identification of products isolated from the cyanamide/MGEBA reaction, the applicability of the proposed mechanism to the dicy/epoxide reaction is confirmed by the presence of products III–V in the dicy/MGEBA reaction mixtures. Alkylated dicys, such as products I and II, were not observed at the temperatures required for the uncatalyzed dicy/MGEBA reaction studies. It is probable that, once formed, these products rapidly undergo further reaction. The rate-controlling step in the uncatalyzed dicy/MGEBA reaction appears to be the initial dicy/epoxide addition, controlled by the slow dissolution and diffusion of dicy. Thus, HPLC observations merely document the gradual accumulation of virtual end products throughout the course of the reaction.

The role of water in the dicy/epoxide reaction mechanism may be complex. The possibility exists that some hydrolysis of the dicy imide bond occurs prior to cyclization, leading to the formation of substituted ureas. As previously discussed, urea/epoxide adducts undergo cyclization reactions similar to that proposed for product III formation. Thus, the further reaction of any hydrolytically generated ureas with MGEBA would ultimately lead to the formation of products IV and V. It is believed that chromatographic peak F in Figure 1 may contain a urea/MGEBA adduct. Although not isolated in pure form, material collected from this peak was observed to decompose into product IV and the monosubstituted analogue of IV (peak A), when heated to 187 °C. Other pathways to product IV formation also exist, as discussed below.

Uneluted Material. Using MGEBA and the isolated products, an attempt was made to correlate HPLC peak areas with product concentration. When detected with a 280-nm source, this relationship was not only found to be linear for all compounds but it was also discovered that peak areas were directly proportional to the concentration of phenyl rings in the eluting compound, regardless of its molecular structure. Thus, it was possible to determine the weight fraction of consumed MGEBA comprising each of the various products in the dicy/MGEBA reaction mixtures. It became immediately evident that a substantial fraction of the consumed MGEBA could not be accounted for by a summation of the several product peaks. It was believed that a product fraction existed that was unelutable by reversed-phase HPLC, either due to reaction with the column packing material or due to its extremely low polarity. Comparison of the SEC chromatogram of an unresolved product mixture with those of the PLC eluted fraction confirmed the existence of this uneluted material. Although individual components could not be isolated, it was possible to collect a fraction of this material by flushing the elutable products of an unresolved mixture through a PLC column with 90% MeOH and then immediately backwashing with 100% THF. An FTIR spectrum of material collected in this manner, shown in Figure 14, reveals a strong carbonyl absorbance band at 1699 cm^{-1}. It can be speculated that this carbonyl is formed via the hydrolysis of either substituted dicy or an intermolecular reaction product of substituted dicy. Heating for extended periods at the temperatures required for dicy/MGEBA reaction results in the apparent partial decomposition of this uneluted fraction, accompanied by the formation of 2-oxazolidones. Probable structures for the uneluted components include ureas, guanyl ureas, or linear urethanes. While little is known about the identity of these uneluted components, it appears that they are more highly substituted than any of the eluting species. As such, they are representative of structures that make a substantial contribution to the cross-link density of a dicy-cured epoxy resin.

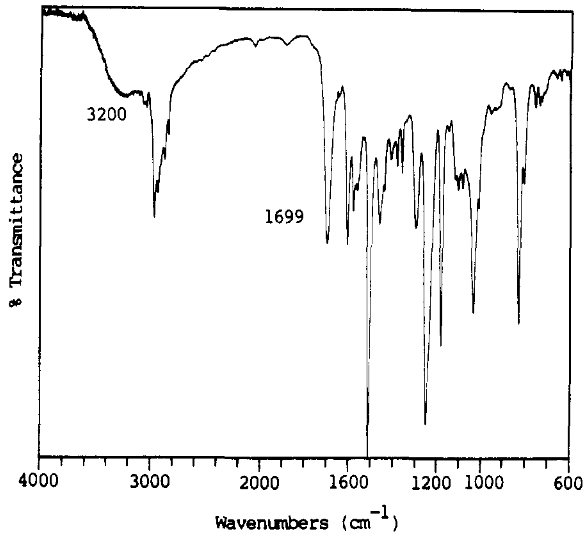


Figure 14. FTIR spectrum of uneluted material.

FTIR Analysis of Unresolved Mixtures. FTIR analyses of the isolated products allows the identification of several spectral features observed during dicy/epoxide cures. Absorbance bands at 2180 and 1570 cm^{-1} are assigned, respectively, to cyano and imide functionalities of substituted dicys. Cyclization shifts these bands to 2205 and 1650 cm^{-1}, respectively. In the curing system, the appearance of these bands is indicative of the formation of structures analogous to product III. Carbonyl bands in the region of 1740–1760 cm^{-1} are indicative of structures analogous to product IV, while those in the region of 1690–1700 cm^{-1}, presumably attributable to urea or guanyl ureas, are indicative of structures analogous to components of the uneluted material. These bands have been observed in FTIR studies of both the base-catalyzed[7] and uncatalyzed[8] dicy cures of epoxy resins. In the present study, base catalysis did not appear to affect the overall mechanism of the dicy/MGEBA reaction. FTIR spectra of unresolved product mixtures formed by the BDMA-catalyzed and uncatalyzed dicy reactions are shown in Figures 15 and 16, respectively. Observed differences appear to be primarily attributable to reaction temperature. The spectrum of the base-catalyzed mixture, reacted at 100 °C, exhibits absorbance bands at 2180 and 1690 cm^{-1}, indicating high concentrations of both alkyl dicys and unelutable products. HPLC analysis of this mixture also reveals evidence in support of high alkyl dicy concentrations. In contrast, no evidence of alkyl dicys is observed in the spectrum of the uncatalyzed mixture, reacted at 160 °C. However, strong bands at 2205, 1740, and 1650 cm^{-1} indicate high concentrations of cyclical products III and IV in these mixtures, formed apparently at the expense of both alkyl dicys and uneluted material. Thus, it appears that cyclization is favored by higher reaction temperatures, in agreement with the observations of Lin et al.[7]

HPLC studies of the cyanamide/MGEBA reaction have shown that cyanamide dimerization is competitive with cyanamide/epoxide addition, even in mixtures containing a large excess of epoxide. In the Zahir study, it is likely that alkyl dicys were also formed in the reaction of cyanamide/PGE mixtures. These mixtures were reacted at 77 °C, which apparently promoted both accumulation

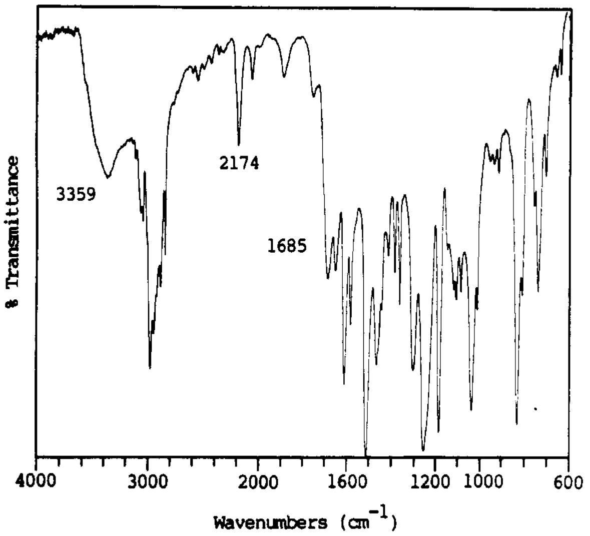


Figure 15. FTIR of unresolved product mixture formed by reacting BDMA-catalyzed 1:6 dicy/MGEBA at 100 °C for 1 h.

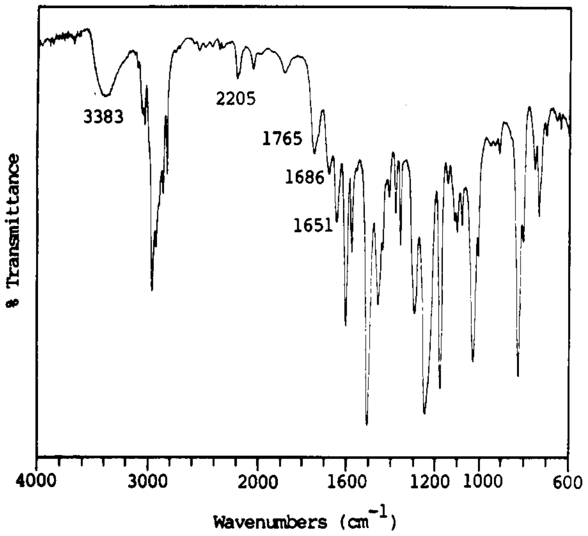


Figure 16. FTIR of unresolved product mixture formed by reacting 1:6 dicy/MGEBA at 190 °C for 1 h.

of alkyl dicys and formation of products analogous to the uneluted species of the dicy/MGEBA reaction, as evidenced by the appearance of a strong absorbance band at 1700 cm^{-1} in FTIR studies of the unresolved cyanamide/PGE product mixture. Only when these mixtures were heated to higher temperatures did Zahir observe the 1740-cm^{-1} band indicative of 2-oxazolidones. Upon reaction of the unresolved mixture with HCl, both the 1700 and 1740-cm^{-1} absorbance bands were observed to increase, supporting the contention that both carbonyl groups are formed via hydrolysis reactions.

Conclusions

The initial dicy/epoxide reaction results in the formation of *N*-alkyl dicyandiamides via simple amine/epoxide addition. Contrary to the mechanism proposed by Zahir, these adducts do not cyclize by hydroxyl/cyano addition but rather by the intramolecular nucleophilic substitution of hydroxyl at the imide functionality, resulting in the elimination of ammonia or alkylamines. In a curing system, the 2-cyanimidooxazolidine formed by this reaction is effectively difunctional and acts as a difunctional epoxy chain extender. Tertiary amines, formed by the further reaction of the generated ammonia and/or amines with epoxide, act as trifunctional cross-linkers. Additional cross-linking is contributed by structures analogous to the as yet unidentified non-HPLC elutable products of the dicy/MGEBA reaction.

Carbonyl generation occurs as a result of the hydrolysis of imide and probably cyano functionalities by water contained in the curing resin. Little is known about the effect of water on the mechanism and kinetics of the dicy/epoxide cure or about the role hydrolysis plays in the formation of structures analogous to the uneluted products of the dicy/MGEBA reaction. However, it is clear that hydrolysis will increase the concentration of available amine functionalities during the cure, resulting in stoichiometric variations. Further, the urea-type structures that may be formed by these hydrolysis reactions will be susceptible to cyclization/elimination reactions similar to those of the *N*-alkyl dicys. Finally, cyclization and hydrolysis reactions occurring subsequent to completion of cure will result in degradation of the cross-linked network and/or introduction of small polar molecules into the cured system.

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Registry No. II, 109748-81-4; III, 109739-57-3; MGEBA, 461-58-5; dicy, 461-58-5; cyanamide, 420-04-2.