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## THE SYNTHESIS AND CHARACTERIZATION OF METAL BINDING POLYMERS CONTAINING 2, 2'-BIIMIDAZOLE

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### ABSTRACT

Epoxides are known to form ring-opened polymer products that have demonstrated improved material strength, high heat stability, and chemical resistance as adhesives, coatings, and molding materials. It has been suggested that imidazoles can be used in the catalysis of this polymerization, and that the pyridyl nitrogen of the imidazole ring participates in epoxy ring-opening and is then incorporated in the polymeric structure. This study was conducted to test this theory of the role of pyridyl nitrogen in the reaction of 1,1'-dihydroxyethyl-2,2'-biimidazole (HEB) and metal-HEB complexes with the diglycidyl ether of bisphenol A (DGEBA). Of particular interest in this study is that HEB also exhibits two alcohol functionalities which are known to induce epoxy ring-opening and that HEB also forms an alkoxide ion adduct which promotes chain growth. DSC and IR were used to monitor the reactions of HEB and its metal complexes with DGEBA. These studies support the conjecture that the pyridyl nitrogen participates in epoxide ring-opening. They also suggest that the pyridyl nitrogen ring-opening is the first reaction, followed by the formation of the alkoxide adduct formation and the hydroxyethyl group etherification. NMR and GPC were employed to further characterize the polymer formed. NMR results varified the proposed polymer structure, and molecular weight determination by GPC showed a high molecular weight, highly cross-linked polymer product.

### INTRODUCTION

Epoxides are known to form epoxide ring-opened polymer products in the presence of various reactive organic compounds such as acids (anhydrides), amines, alcohols and phenolics. These polymer products have found significant utility as adhesives, polymeric coating materials, and

molding materials and have demonstrated improved material strength, high heat stability, and chemical resistance in these capacities.

Among known catalysts for the ring-opening and subsequent homopolymerization of epoxy compounds are imidazoles. Imidazoles are added to initiate esterification reactions in epoxy-anhydride systems, are used to catalyze specific epoxy-phenolic hydroxyl reactions, and are used as hardeners in a variety of commercial epoxy resin systems.

Previous investigations [1-3] on epoxy/imidazole systems have put forth some general conclusions about the formation of epoxy/imidazole adducts. As can be seen in Figure 1, these conclusions say that for a 1:1 epoxy/imidazole reaction in which the imidazole is a 1-unsubstituted imidazole, both a 1:1 hydroxide (OH) adduct and a 2:1 alkoxide (O<sup>-</sup>) adduct are formed. In these reactions, the imidazole becomes a part of the polymeric structure. In fact, in the formation of the 2:1 alkoxide (O<sup>-</sup>) adduct it has been suggested that the pyridyl nitrogen of the imidazole ring participates in epoxy ring-opening and is then incorporated in the polymeric structure.

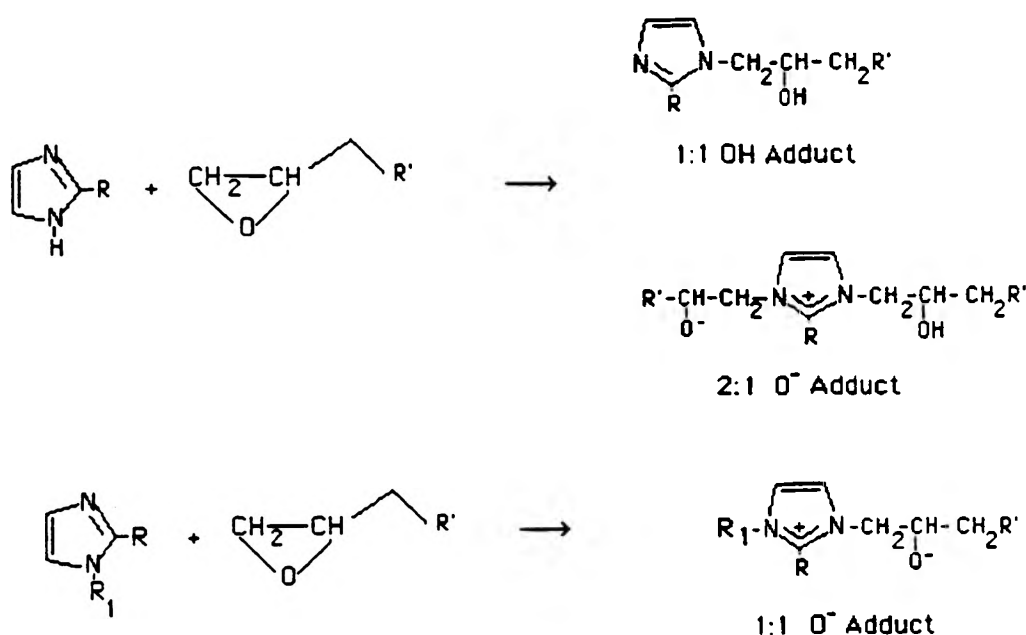


Figure 1. Imidazoles as Epoxy Catalysts.

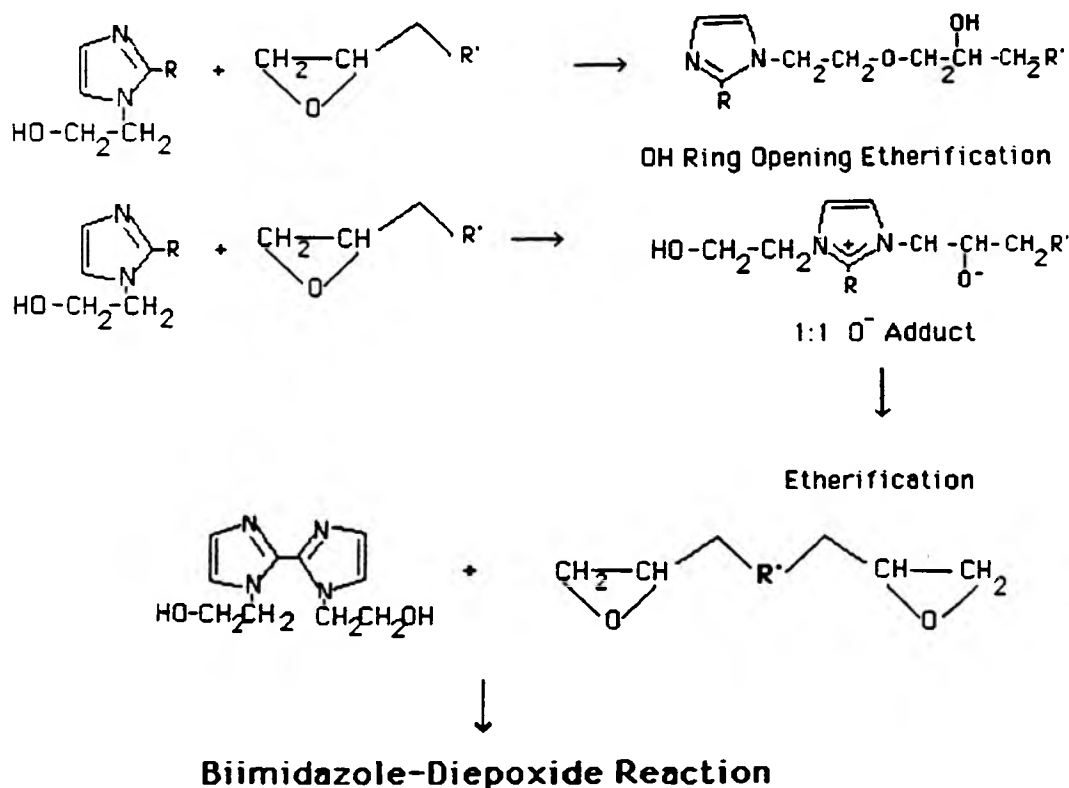


Figure 2. 1-Substituted Imidazole Epoxide Catalyst.

In a similar fashion, the formation of a 1:1 alkoxide (O<sup>-</sup>) adduct is expected for 1-substituted imidazole/epoxide reactions. In this case the pyridyl nitrogen is again utilized in the adduct formation.

Suppose the 1-substitution on the imidazole is a hydroxyl ethyl group as suggested by Figure 2. Then one must not only consider the previously mentioned 1:1 alkoxide adduct formed by epoxy ring-opening by the pyridyl nitrogen of imidazole, but one must also consider the possibility of the formation of a 1:1 imidazole/hydroxy ether adduct via hydroxyethyl ring-opening.

Subsequent to the formation of these adducts, which have been proposed to occur rapidly and initially, is the etherification reaction, which results in chain growth via OH-etherification and O-etherification reactions.

Another important consideration is that the alkoxide ion is highly reactive, and once placed in such a situation, will promote the O-etherification reaction.

The question posed by this phase of the investigation is: "is it possible to observe some discernment in the reaction of 1,1'-dihydroxyethyl-2,2'-biimidazole (HEB) with diepoxides?" For example, can the formation of the imidazole pyridyl nitrogen-epoxy adduct and the formation of the hydroxyethyl-epoxy adduct be observed? Can the proposed etherification reactions be observed? And what is the metal ion effect when it is used to block the pyridyl nitrogen sites?

I plan to discover the role of HEB, nickel-HEB, and cobalt-HEB (HEB, Ni-HEB, and Co-HEB respectively), complexes in reactions with the diglycidyl ether of bisphenol A, or DGEBA. If it is expected that there is an ordering of reactive groups for this and related reactions, then one might expect that the thermal monitoring of this reaction as a function of temperature may provide insight to what actually occurs.

In this particular case, the reaction order was expected to proceed as follows: the epoxide ring opening with the formation of the imidazole ring pyridyl nitrogen-epoxy alkoxide adduct; and the more rapid reaction of the alkoxide adduct with epoxide groups as well as the hydroxyethyl group ring-opening etherification.

It is proposed that if the pyridyl nitrogen sites are occupied by a transition metal ion, then the principle reaction should be the hydroxyethyl group ring-opening etherification.

## EXPERIMENTAL

**Materials and Reagents:** The epoxide used in this study, the diglycidyl ether of bisphenol A (DGEBA), was obtained from DAJAC Laboratories, Incorporated and was utilized without further purification.

**Purification of HEB:** The first problem confronted in this experiment was the task of purifying the 1,1'-dihydroxyethyl-2,2'-biimidazole. Testing a sample to determine its purity entailed a simple thin layer chromatographic analysis. First the sample of the crude HEB was dissolved in methanol and was dotted on a 1x6 inch thin layer chromatography silica plate. Once dry, it was placed in a covered graduated cylinder and allowed to develop for approximately 90 minutes to 2 hours in an 8:3:1 hexane : propanol : ethanol solvent mixture. The crude HEB was found to resolve into two basic components: mono-substituted HEB and the desired di-substituted HEB.

It was decided to employ flash chromatography in the purification process. After a lot of procedures were tried and sample purity was tested by the procedure outlined above, a sketchy method of purification was developed that gave consistently pure HEB. First, approximately 0.5 g of the crude HEB was dissolved in methanol. This often required a little heating, and usually, there was some insoluble solid present that was assumed to be impurities and was filtered out of the solution. Second, the flash chromatography column was rinsed with 8:3:1 hexane : propanol : ethanol solvent mix. Next, the dissolved HEB was introduced to the column and pumped down into the silica. Then the HEB mixture was chased through with the 8:3:1 solvent mix until pure white silica became discolored. At this point, the solvent was switched to methanol and the methanol was pumped through the column. A distinct yellow band was observed to form and move slowly down the silica column. This band contained the pure, golden HEB. The methanol wash was continued until the band reached the bottom of the column. Now, in a separate vial, the pure product was able to be collected by continuing the methanol strip until the yellow band was gone, and approximately 30 mL of the liquid was collected beyond that point. Finally, the methanol was allowed to evaporate in a beaker so that only the pure HEB sample remained.

**Thermal Analysis:** From the purified HEB, Ni-HEB, and Co-HEB samples, 1:1 molar HEB : DGEBA reaction samples were prepared in vials. These samples were weighed out on a Mettler PM460 Tare Scale. They were then mixed with a spatula, and stored under Argon gas in a 6° to 8° Celsius refrigerator. These precautions were taken to ensure a moisture and heat-free atmosphere so that no reactions occurred during storage.

Thermal analysis of the samples involved monitoring by Differential Scanning Calorimetry, or DSC. Five milligrams of the previously prepared reaction mixture were placed in aluminum sample pans and covered with a lid. These samples were placed in the Perkin-Elmer DSC-4 and scanned between 50° and 250° Celsius under a nitrogen atmosphere at a heat rate of 20 degrees per minute. They were then analyzed and sent to the printer. Four samples of each of the three reaction mixtures were ran to ensure reproducibility.

**Fourier Transform Infrared Spectroscopy:** A thin film of the HEB reaction mixture (prepared as described in the thermal analysis section) was cast with MEK onto each of three NaCl salt plates according to the procedure used by Heise and Martin [3]. One plate was not heated, one was

heated for five minutes and the third was heated for 20 minutes in a 180° oven. They were then all quenched cool in a 6° to 8° C refrigerator, and, once cool, were scanned by a Perkin-Elmer Model 1750 Fourier transform infrared spectrometer, or FTIR, under a dry air purge. Peak assignments and percent transmittances were printed out for each plot. The transmittance peaks were identified according to the previous work by Stevens [4].

This procedure was repeated for the NiHEB and the CoHEB reaction mixtures.

**Nuclear Magnetic Resonance Spectroscopy:** A well mixed 1:1 molar HEB : DGEBA sample was prepared in an NMR tube. The reaction mixture was cooked in a 180° oven for 20 minutes and allowed to cool. DMSO was added to the NMR tube, partially dissolving a portion of the polymer product. NMR spectra were obtained for the polymer with a JEOL FX-100 Fourier transform nuclear magnetic resonance spectrometer at room temperature, using TMS as an external standard.

This procedure was repeated for the NiHEB and the CoHEB reaction mixtures.

**Gel Permeation Chromatography:** GPC samples were prepared by mixing a 1:1 molar HEB : DGEBA sample in a sample vial, cooking the sample for 20 minutes in a 180°C oven, and then adding enough DMF to form a .3% solution (given that all the sample had dissolved). The molecular weights of the soluble portions were measured with a modified-component high pressure liquid chromatography (HPLC) system which was calibrated with narrow molecular weight distribution polystyrene samples.

This procedure was repeated for the NiHEB and the CoHEB reaction mixtures.

## RESULTS AND DISCUSSION

**Thermal Analysis:** The monitoring by DSC of HEB, NiHEB, and CoHEB with DGEBA is illustrated in Figure 3. The endotherm for the HEB-DGEBA reaction is presumably due to the heat of reaction required for the pyridyl nitrogen to initiate ring-opening. The wide exotherm thereafter, at about 150°C, is thought to account for the alkoxide and hydroxyethyl reactions with epoxide. Compare this to the DSC scans obtained for the reactions of NiHEB and CoHEB with DGEBA, which clearly show a single exotherm at approximately 200°C and 250°C respectively. Since, in the case of the

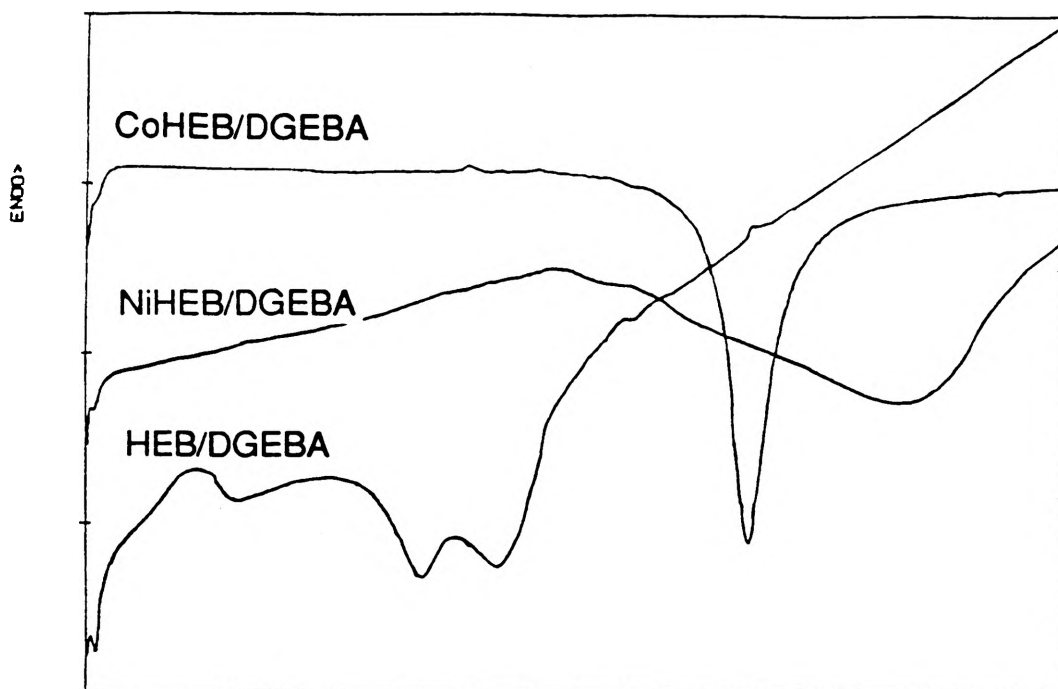


Figure 3. DSC Monitoring of HEB, NiHEB, and CoHEB/DGEBA Reactions

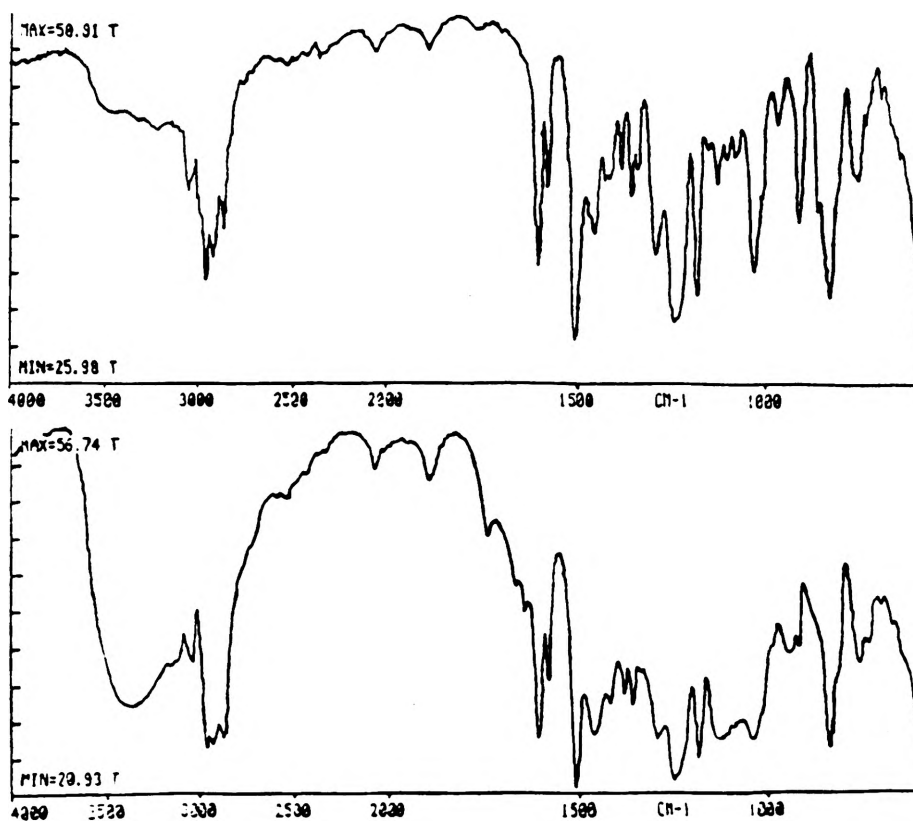


Figure 4. IR Spectra of HEB/DGEBA Before and After Polymerization



metal HEB molecules, the pyridyl nitrogen has been blocked, this single peak is due to the reaction of the hydroxyethyl group with the diepoxide.

**Fourier Transform Infrared Spectroscopy:** In the next phase of the experiment, the three samples of each reaction mixture were heated at time intervals of 0, 5, and 20 minutes in a 180° C oven and scanned by FTIR after each period. The intention was to catch the reaction in various stages towards completion. The change in the reaction mixture, however, could be seen best when comparing the 0 and 20 minute samples of each reactant/product pair.

The infrared examination of the mixture of HEB and DGEBA before the reaction is shown at the top of Figure 4. The epoxy peak can be seen here at approximately 916  $\text{cm}^{-1}$ , and at the end of the 20 minute period, the scan for which is shown at the bottom of this figure, the reaction is completed and the epoxide is gone as expected. Note also the band assignments at 1670, the C=N, and the broad band appearing in the 3200 to

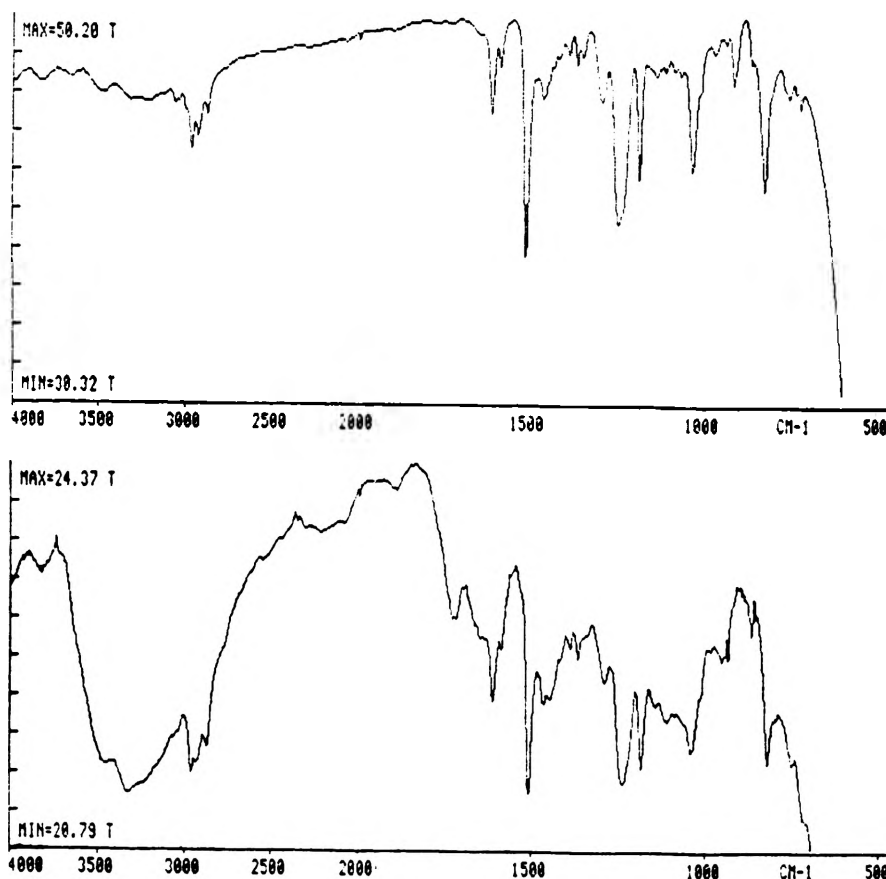


Figure 5. IR Spectra of NiHEB/DGEBA Before and After Polymerization

3400  $\text{cm}^{-1}$  region, the N-H stretching region of the 1-substituted imidazole, as proof of the incorporation of HEB into the polymeric network. This band is especially exciting since the substance scanned initially is believed to be only DGEBA since the reaction mixture was rather heterogeneous. The growth of this peak from the initial to the final scans is further proof of the incorporation of the biimidazole in the polymer.

The FTIR scans in Figures 5 and 6 show similar results for the reaction of NiHEB and CoHEB with DGEBA. Before heating for 20 minutes in the 180° C oven, an epoxy peak can be observed at 915  $\text{cm}^{-1}$ , but after the heating, the peak is gone and the reaction is complete. These FTIR results help to justify that the expected is occurring, and it is producing an epoxy ring-opened product.

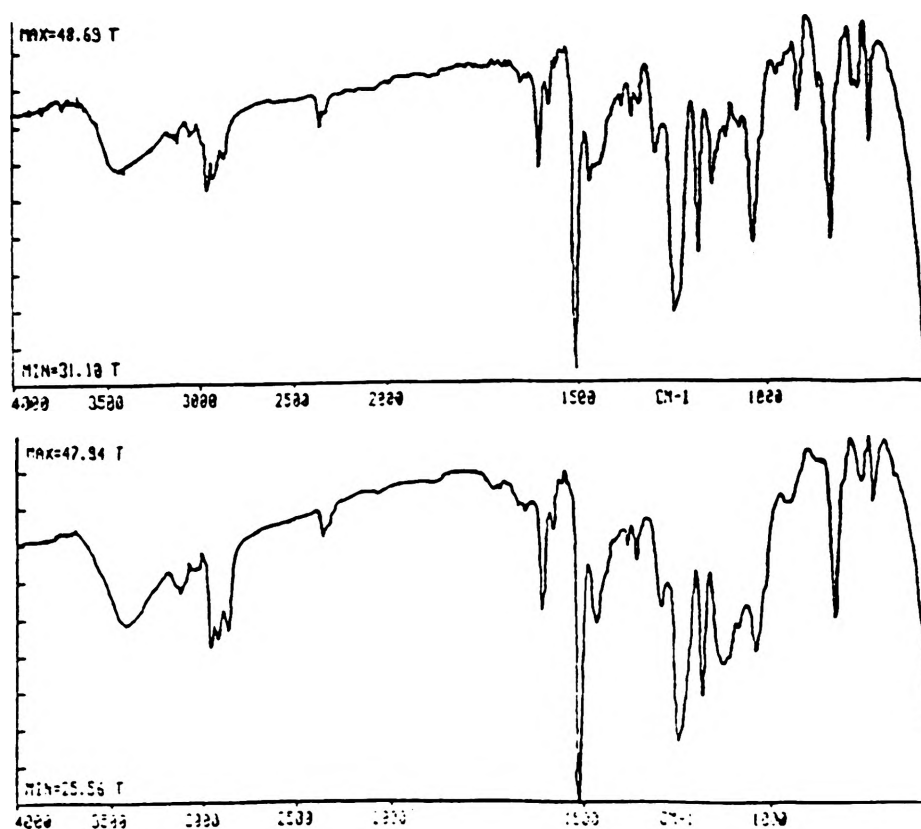


Figure 6. IR Spectra of CoHEB/DGEBA Before and After Polymerization

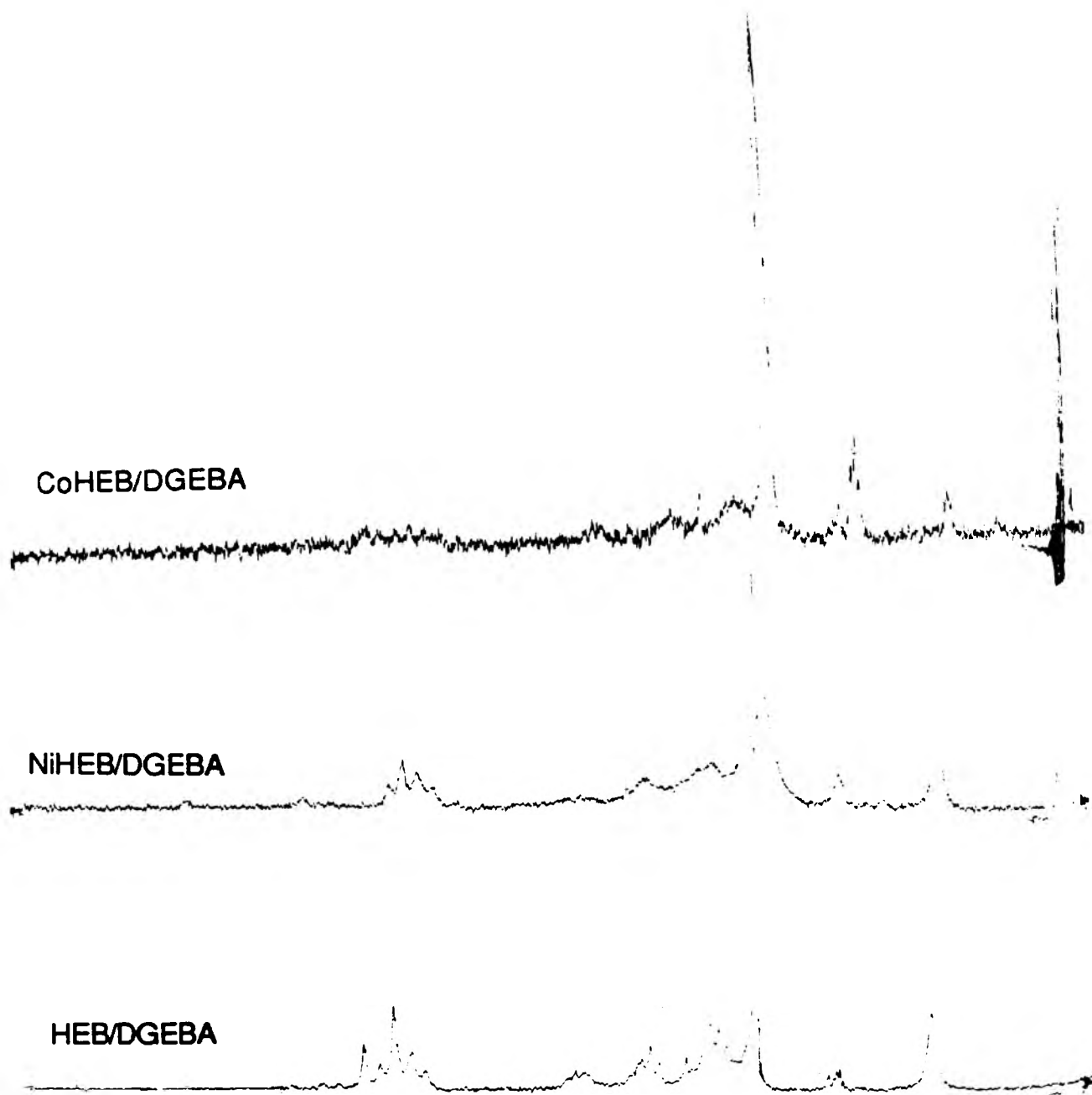


Figure 7. NMR Spectra of HEB, NiHEB, and CoHEB/DGEBA Reactions

Once again the C=N can be observed at 1670 and the broad 1-substituted imidazole band can be observed between 3200 and 3400 cm<sup>-1</sup> as the metal HEB is incorporated into the final polymeric structure.

**Nuclear Magnetic Resonance Spectroscopy:** The proton NMR analysis of the HEB/DGEBA, the NiHEB/DGEBA, and the CoHEB/DGEBA reaction products is illustrated in Figure 7. Chemical shifts due to various functional groups such as those observed at approximately 1.3ppm (epoxy), 3.1ppm (methyl), 3.6ppm (o-methylene), 4.2ppm (N-methylene), and 6.6-7.2ppm (aromatic) proved that the suspected polymer products were being formed.

**Gel Permeation Chromatography:** The HEB/DGEBA polymer was tested and proved to be insoluble in the eluting solvent, DMF. This is proof of a high molecular weight, highly crosslinked polymer.

### CONCLUSIONS

So far, by blocking the pyridyl nitrogen sites of HEB with nickel and cobalt, support has been given to the conjecture that the pyridyl nitrogen participates in epoxide ring-opening. An order of reaction for the different functional groups has also been proposed. The product proved to be polymeric in nature, and qualitative nuclear magnetic resonance proved that the expected reactions were occurring by observation of the expected functional group peaks. Finally, the polymer has proven to be minimally soluble in DMF so it is assumed to be a high molecular weight, highly crosslinked species.

Future plans include the expansion of the study to reactions with other diepoxides to witness if the reaction proceeds in a similar manner as described here. Also, this polymer needs to be produced in larger quantities and tested for macromolecular properties such as polymer hardness and adhesion. Such tests may prove this highly crosslinked polymer to be an improvement over currently used epoxy systems in the epoxy paint industry.

### **ACKNOWLEDGEMENTS**

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