

01 Apr 1991

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

Renee Proctor

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 in reactions 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. I used DSC and IR 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.

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 investigations¹⁻³ 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-) 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-) 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.

In a similar fashion, the formation of a 1:1 alkoxide (O-) 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.

Imidazoles as Epoxy Catalysts

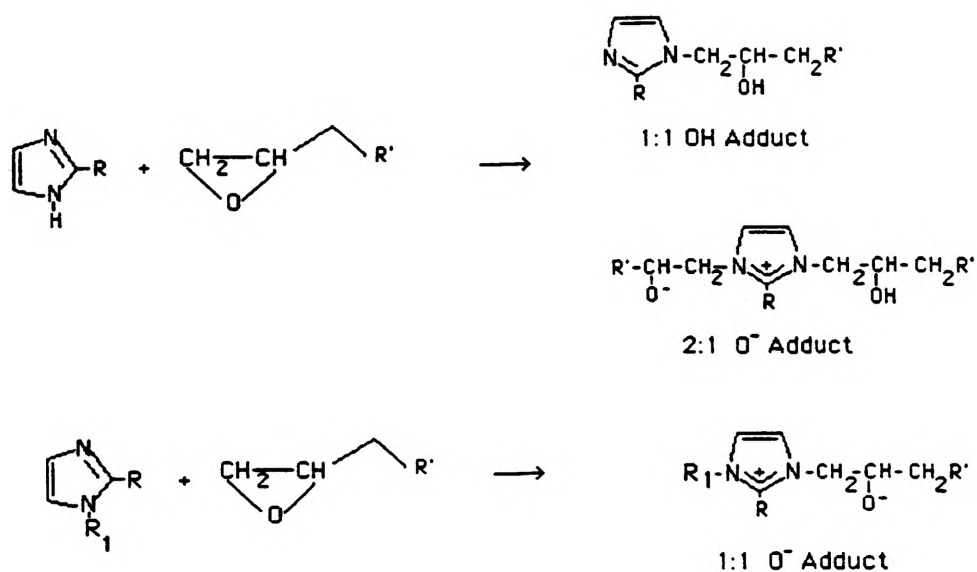


FIGURE 1

1-SUBSTITUTED IMIDAZOLE EPOXIDE CATALYST

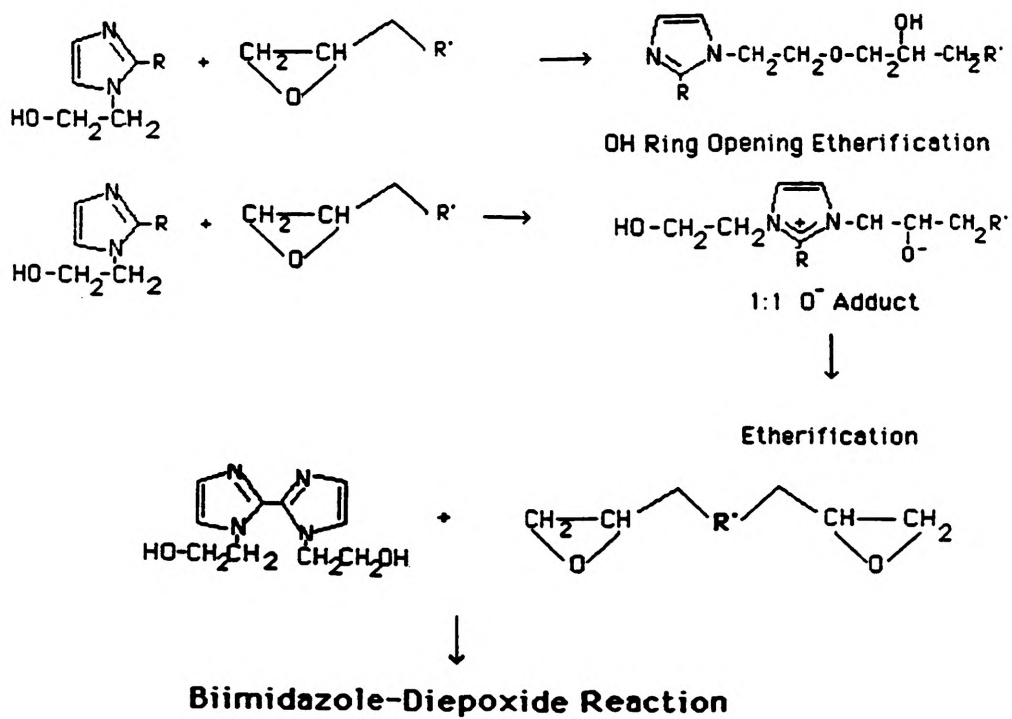


FIGURE 2

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 and cobalt-HEB, or Co-HEB, 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 site is occupied by a transition metal ion, then the principle reaction should be the hydroxyethyl group ring-opening etherification.

Experimental Section

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 5 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.

From the purified HEB and the 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 DSC and scanned between 50° and 250° Celsius at a heat rate of 20 degrees per minute. They were then analyzed and sent to the printer. Four samples of each of the two reaction mixtures were run to ensure reproducibility.

Next, a thin film of the HEB reaction mixture and the Co-HEB reaction mixture was spread on NaCl salt plates. These plates were first heated in a 70°C oven for 2 minutes. They were then quenched cool in the 6° to 8° C oven, and, once cool, were scanned by a Fourier Transform Infrared Spectrometer, or FTIR. The plates were heated in the same oven for 5, 15, and 90 minutes respectively, cooled, and scanned each time. After these tests, the salt blocks were placed in a 185° C oven for 15 minutes. They were once again quench cooled in the refrigerator and scanned on the FTIR. Peak assignments and percent transmittances were printed out for each plot.

Results and Discussion

The monitoring by DSC of HEB with DGEBA 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 scan obtained for the reaction of CoHEB with DGEBA, which clearly shows a single exotherm at approximately 200°C. Since, in the case of CoHEB, the pyridyl nitrogen has been blocked, this peak is due to the reaction of the hydroxyethyl group with the diepoxide.

In the next phase of the experiment, the sample was heated for four different time intervals in a 70° C oven and scanned by FTIR after each period. The intention was to catch the reaction in various stages towards completion. However, little to no change was actually observed. The samples were then heated in the 185° oven for 15 minutes to prove that the reaction reached completion as expected through observation of the epoxy peak.

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 cm^{-1} , and at the end of the 15 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 3400 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.

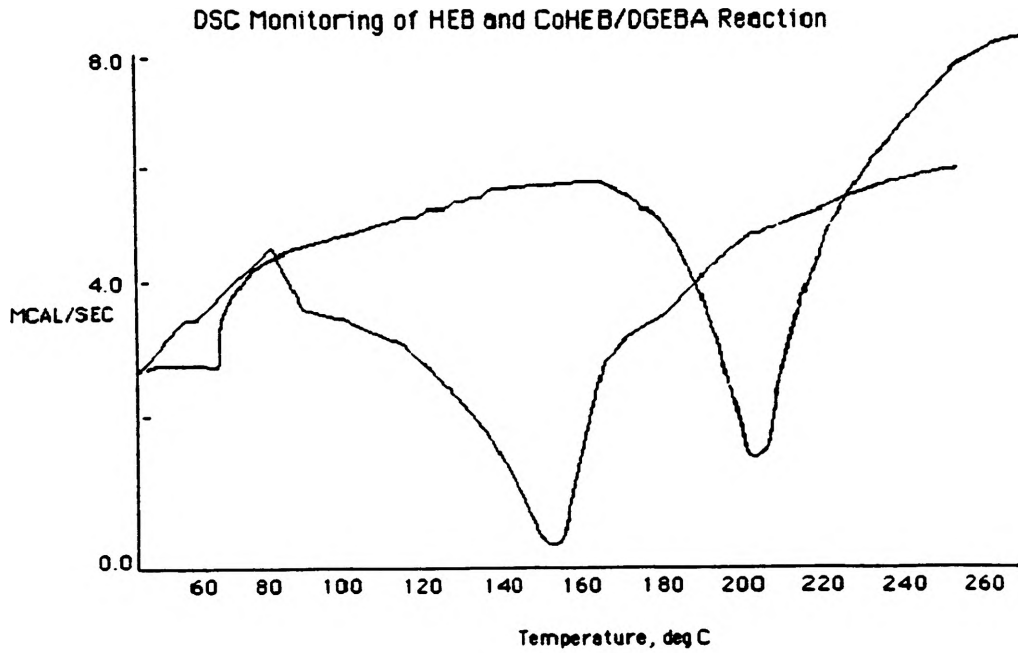


FIGURE 3

Infrared Spectra of HEB/DGEBA Before and After Polymerization

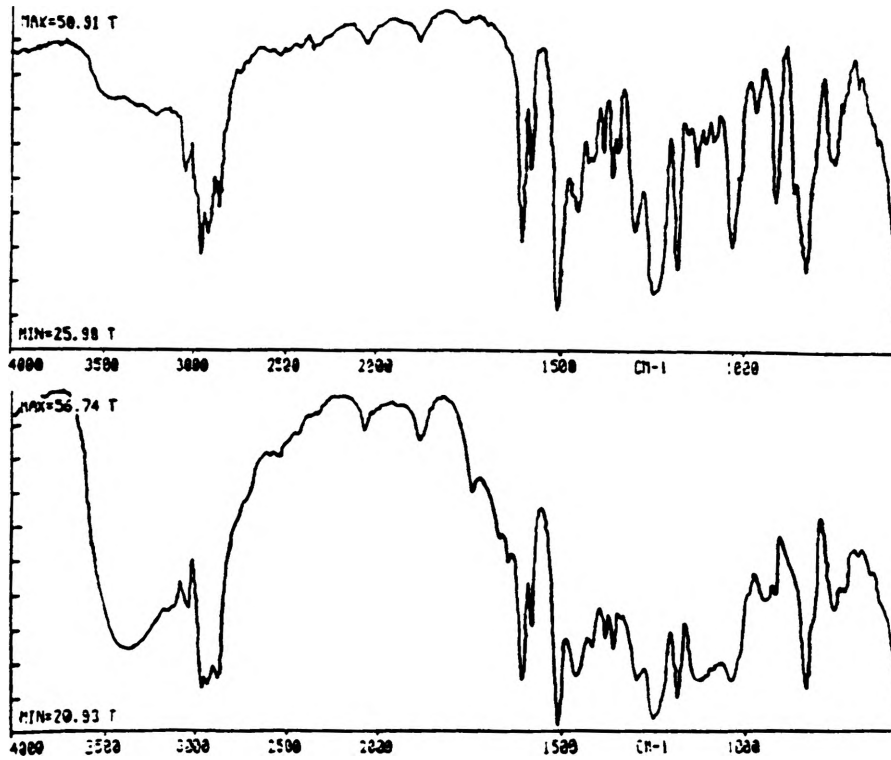


FIGURE 4

The FTIR scan in Figure 5 shows similar results for the reaction of CoHEB with DGEBA. Before heating for 15 minutes in the 185° C oven, an epoxy peak can be observed at 915 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.

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⁻¹ as the HEB is incorporated into the final polymeric structure.

Conclusions

So far, by blocking the pyridyl nitrogen sites of HEB with 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. Further thermal analyses with a slower scanning rate on the Differential Scanning Calorimeter need to be run in order to differentiate among the steps even further. That is, with a slower heating rate, perhaps the wide exotherm containing the reaction of both the alkoxide adduct with epoxide groups as well as the hydroxyethyl group ring-opening etherifications can be separated into its two component reactions so that a definite order can be assigned to these reactions. Also, a method to stop the reaction at different stages by cold quenching needs to be developed so that further differentiation and characterization of the steps of this reaction may be made with FTIR. Characterization of the final polymer products of the HEB/DGEBA and the CoHEB/DGEBA reactions will be made by Nuclear Magnetic Resonance and Gel Permeation Chromatography analyses.

Future plans include the study of the effects of other metal ions, such as nickel and copper, on the reaction. Also, the study will be expanded to reactions with other diepoxides to witness if the reaction proceeds in a similar manner as described here.

References

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Infrared Spectra of CoHEB/DGEBA Before and After Polymerization

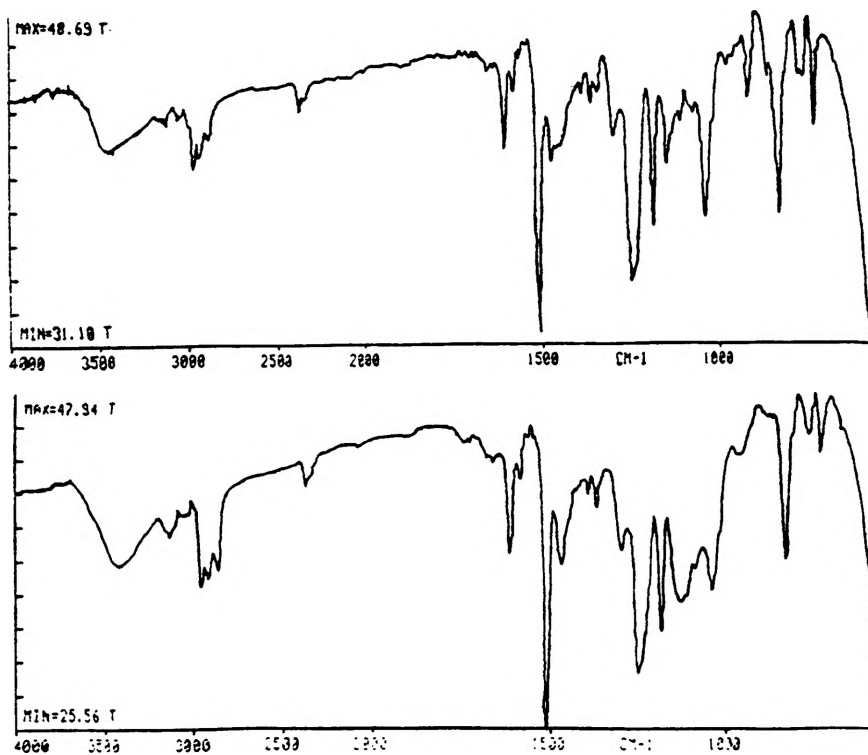


FIGURE 5